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Water/Carbon Dioxide Phase Equilibria Using Thermodynamic Perturbation Theory

W.P. Yong and M. Awang

Department of Petroleum Engineering, Faculty of Petroleum Engineering and Geoscience,
Universiti Teknologi PETRONAS, Tronoh, 31750, Perak, Malaysia

Abstract: The Cubic Plus Association (CPA) and the Statistical Associating Fluid Theory (SAFT) are theoretically derived based on perturbation theory using Wertheim theory by considering the effect of hydrogen bonding on thermodynamic properties of associating fluids. These EoS are applied to predict the phase equilibrium of pure water and carbon dioxide system at different temperatures and pressures. A comparison has been made between those EoS and the widely used cubic EoS such as Soave-Redlich Kwong (SRK) and Peng-Robinson (PR) EoS. Satisfactory predictions are obtained for CPA and SAFT EoS and the analysis of results show that these theoretically derived models can successfully predict the pure water and carbon dioxide system even with zero binary interaction parameter.

Key words: Equation of state, cubic plus association, statistical associating fluid theory

INTRODUCTION

Phase equilibria description is important in chemical engineering and petroleum engineering applications such as refinery, petrochemical, fluid separation and gas injection processes. The systems become complicated with the presence of associating compounds with hydrogen bonding like water, methanol and glycols at low and high pressure and temperature.

Soave-Redlich Kwong EoS (Soave, 1972) is suitable for light hydrocarbons (C_1 - C_{10}) and simple water handling and Peng-Robinson EoS (Peng and Robinson, 1976) is superior in predicting liquid densities especially for nonpolar materials. However, these cubic EoS were developed for hydrocarbon mixtures prediction. In the presence of water, although one can argue that water is inert phase, its mutual solubility with carbon dioxide becomes significant once it reaches high temperature and pressure. At the same time, the conventional cubic EoS cannot satisfactory predict systems near critical region.

To describe the systems containing associating compounds, empirical/semi-empirical modifications of cubic EoS or more theoretically-based EoS models that account for association are needed. For example, mixing rules (Huron and Vidal, 1979; Wong and Sandler, 1992) can be applied to combine with cubic EoS to describe polar compounds and asymmetric systems. However, those mixing rules are semi-empirical and their prediction results can be questionable. Based on numerous investigations in finding more reliable EoS for associating fluids, more theoretical insights EoS have been derived

from chemical theory (Ikonomou and Donohue, 1986), from perturbation theory with SAFT EoS (Chapman *et al.*, 1990; Huang and Radosz, 1991), the Group-Contribution-Associating (GCA) EoS (Gros *et al.*, 1996) and CPA EoS (Kontogeorgis *et al.*, 1996) and from the lattice/quasi-chemical theory (Panayiotou and Sanchez, 1991).

In this study, SRK, PR, SAFT and CPA-PR EoS are applied to model, the Vapor-Liquid Equilibria (VLE) and Liquid-Liquid Equilibria (LLV) of water/carbon dioxide system at specific temperatures and pressures. The performance of SAFT and CPA-PR EoS for the correlation of pure water and carbon dioxide phase equilibrium is examined and compared with PR and SRK EoS.

CUBIC PLUS ASSOCIATION-PENG ROBINSON (CPA-PR EoS)

Cubic Plus Association-Peng Robinson (CPA-PR EoS) was developed by Kontogeorgis *et al.* (1996) and it has the physical term from PR EoS and associating term from SAFT EoS where the association term based on Wertheim (1984a, b, 1986a, b, c) first-order thermodynamic perturbation theory assumptions. The CPA-PR EoS can be expressed mathematically by:

$$p = \frac{RT}{V-b} - \frac{aa}{V(V+b)+b(V-b)} - \frac{1}{2} \left(\frac{RT}{V} \right) \left(1 + \frac{1}{V} \frac{\partial \ln g}{\partial \left(\frac{1}{V} \right)} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

Where:

- p = System pressure (psi)
- T = System temperature (°R)
- R = Gas constant (10.73 psi-ft³/lb-mol °R)
- V = Molar volume (ft³/mol)
- a = Attraction parameter
- b = Repulsion parameter
- α = Temperature correction parameter
- X_i^a = Fraction of A-sites of molecule i that are not bonded with other active sites
- x_i = Mole fraction of component i

CPA-EoS has pure-compound parameters that accounts for non-associating compounds and associating compounds. The a, b and α parameters for PR EoS are given by:

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (2)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha = \left[1 + m \left(1 - \sqrt{T_r} \right) \right]^2 \quad (4)$$

Where:

- p_c = System pressure (psi)
- T_c = System temperature (°R)
- T_r = Reduced temperature (T/T_c)
- m = 0.3796 + 1.54226ω - 0.2699ω³

or:

$$m = 0.379642 + 1.48503\omega - 0.1644\omega^2 + 0.016667\omega^3 \text{ (for } \omega > 0.49) \quad (5)$$

where, ω is acentric factor of pure substance.

In association term in Eq. 1, X_{Ai} can be calculated by:

$$X_i^A = \frac{1}{1 + \left(\frac{1}{V} \right) \sum_j X_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (6)$$

Where:

- B_j = Summation over all sites
- Δ^{A_iB_j} = Association (binding) strength between site A on molecule i and site B on molecule j with:

$$\Delta^{A_i B_j} = g(V)^{ref} \left[\exp \left(\frac{\epsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (7)$$

Table 1: CPA parameters for pure fluids

Fluid	a	b	ω	ε	β
CO ₂	3.9631	0.0267	0.2200	0.0000	0.0000
H ₂ O	4.2562	0.0160	0.0000	2258.6	0.0185

Where:

- ε^{A_iB_j} = Association of energy between site A of molecule I and site B of molecule j
- β^{A_iB_j} = Volume of interaction between site A of molecule I and site B of molecule j
- g(v)^{ref} = Contact value of the radial distribution function for the reference fluid

Radial distribution function can be expressed as:

$$g(V)^{ref} = \frac{n - \eta}{2(1 - \eta)^3} \quad (8)$$

$$\eta = \left(\frac{1}{4V} \right) b \quad (9)$$

where, η is reduced fluid density.

For the extension of CPA-PR EoS to mixtures, mixing rules are needed for PR EoS parameters. Combining rules for the association energy and volume parameters are needed between different associating molecules with i ≠ j. In this case, water is modeled as (3B) molecules based on terminology of Huang and Radosz (1991). The parameters for all associating and inert compound used in this study are shown in Table 1.

STATISTICAL ASSOCIATING FLUID THEORY (SAFT-EoS)

The Huang and Radosz (1991) developed the SAFT EoS using Chapman *et al.* (1990) general statistical associating fluid theory approach based on Wertheim (1984a, b, 1986a, b, c). The SAFT EoS is expressed in terms of residual Helmholtz energy a^{res} per mole with a^{ideal} ideal gas Helmholtz energy per mole and the sum of another three terms that represent different intermolecular forces contribution. The three terms are a^{seg}, segment-segment interaction forces with hard-sphere repulsive and dispersion interactions, a^{chain}, covalent chain-forming bonds forces among the segments and a^{assoc}, site-site specific interactions forces among segments. The general expression of those Helmholtz energies is given by:

$$a^{res} = a^{ideal} + a^{seg} + a^{chain} + a^{assoc} \quad (10)$$

The segment Helmholtz energy a^{seg}, per mole of molecules, is expressed as:

$$a^{seg} = m a_0^{seg} \quad (11)$$

Where:

- a_0^{seg} = Residual Helmholtz energy of nonassociated spherical segments (per mole of segments)
- m = Segment number

The a_0^{seg} is the summation of hard sphere and dispersion parts where:

$$a_0^{seg} = a_0^{hs} + a_0^{disp}$$

Based on Carnahan and Starling (1969), the hard sphere term, a_0^{hs} is proposed as:

$$\frac{a_0^{hs}}{RT} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \quad (12)$$

$$\eta = \tau \rho m v^0 \quad (13)$$

$$v^0 = \frac{\pi N_{Av}}{6\tau} d^3 \quad (14)$$

$$v^{00} = \frac{\pi N_{Av}}{6\tau} \sigma^3 \quad (15)$$

$$d = \sigma \left[1 - C \exp \left[\frac{-3u^0}{kT} \right] \right] \quad (16)$$

$$u = u^0 \left[1 + \frac{e}{kT} \right] \quad (17)$$

Where:

- η = Reduced fluid density
- τ = 0.74048
- ρ = Molar density (mol/Å³)
- m = Segment number
- v^0 = Temperature dependent segment molar volume mL mol⁻¹ of segments
- N_{av} = Avogadro number
- d = Effective segment diameter (temperature dependent)
- v^{00} = Temperature independent segment molar volume (mL mol⁻¹ of segments)
- σ = Temperature independent segment diameter (Å)
- $\frac{u^0}{k}$ = Temperature independent dispersion energy of interaction between segments (K)
- C = Integration constant ($C \approx 0.12$)
- $\frac{e}{k}$ = Constant related to Pitzer's acentric factor and the critical temperature

The dispersion term is a power series fitted by Alder *et al.* (1972) and it is given by:

$$\frac{a_0^{disp}}{RT} = \sum_i \sum_j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \quad (18)$$

where, D_{ij} is universal constants.

Based on Chapman *et al.* (1990), both chain and association terms are given by:

$$\frac{a^{chain}}{RT} = (1-m) \ln \frac{1 - \frac{1}{2}\eta}{(1-\eta)^3} \quad (19)$$

$$\frac{a^{assoc}}{RT} = \sum_A \left[\ln X^A - \frac{X^A}{2} \right] + \frac{1}{2}M \quad (20)$$

With:

$$X^A = \frac{1}{[1 + N_{Av} \sum_B \rho X^B \Delta^{AB}]} \quad (\text{summation over all sites: A, B, C, ...}) \quad (21)$$

$$\Delta^{A_i B_j} = g(d)^{seg} \left[\exp \left(\frac{\epsilon^{AB}}{kT} \right) - 1 \right] (\sigma^3 k^{AB}) \quad (22)$$

$$g(d)^{seg} \approx g(d)^{hs} = \frac{1 - \frac{1}{2}\eta}{(1-\eta)^3} \quad (23)$$

Where:

- M = Number of association sites on each molecule
- X^A = Fraction of A-sites of molecule i that are not bonded with other active sites
- \sum_A = A sum over all associating sites on the molecule
- Δ^{AB} = Association (binding) strength
- N_{Av} = Avogadro's number
- $g(d)^{seg}$ = Segmental radial distribution function

The temperature independent segment diameter σ which can make k^{AB} becomes dimensionless from Eq. 22 can be obtained by rearranging Eq. 15 as follow:

$$\sigma = \left[\frac{6\tau}{\pi N_{Av}} v^{00} \right]^{1/2} \quad (24)$$

Up till recently, various modified versions of SAFT like VR-SAFT (Gil-Villegas *et al.*, 1997) have been developed. Some of the terms in SAFT are similar and explained in CPA EoS previously. Same like CPA EoS, water is modeled as (3B) molecules. The terminology of Huang and Radosz (1991) is used for association schemes. The parameters for all associating and inert compound used in this work are taken from Pfohl *et al.* (1998) as shown in Table 2.

Table 2: SAFT parameters for pure fluids

Fluid	u_0/k	v_{00}	m	ϵ^A	κ^A	η/k
CO ₂	216.08	0.0136	1.417	0	0	40
H ₂ O	574.96	0.0123	1.000	1940.4	0.0117	1

METHODOLOGY

Data collection: Water/carbon dioxide VLE and LLE experimental data have been collected from Todheide and Franck (1963) at 573.15 K, Wiebe and Gaddy (1939) at 323.15 and 304.19 K, Muller *et al.* (1988) at 373.15 K and Pfohl *et al.* (1998) at 373.15 K.

Modeling software: The program PE (Phase Equilibria) (Pfohl *et al.*, 1998) has been applied to predict the water/carbon dioxide phase equilibria. The PE was developed by Professor Brunner’s research group at the Technical University of Hamburg-Harburg starting in 1985 to correlate phase equilibria especially those at high pressure that are related to gas-extraction processes. The PE offers around forty different equations of state with up to seven different mixing rules for correlating phase equilibria.

Sensitivity analysis: There are a lot of uncertainties during phase equilibria calculations since most of the parameters are correlated empirically from experimental data. These parameters include critical pressure, critical temperature, vapor pressure and its densities, acentric factor, EoS parameters and interaction parameters.

In this study, a sensitivity analysis has been conducted for the uncertain interaction parameters. The binary interaction parameters have been set to zero interaction parameters; interaction parameters based on literature (Pfohl *et al.*, 1998) and optimized interaction parameters.

RESULTS AND DISCUSSION

As mentioned previously, a sensitivity analysis has been conducted with three different sets of binary interaction parameters for PR, SRK and CPA-PR EoS and SAFT EoS. The main focus of the sensitivity analysis is to optimize binary interaction parameters generated from PE software. The optimum representation of phase equilibria in mixtures for EoS, mixing rule and pure component parameters depends on correct choice of mixture parameters, especially when the initial predictions for the system were not good.

Based on predicted data, the optimized binary interaction parameters match satisfactorily with experimental data. At different temperatures, the CO₂ solubility in H₂O is increasing with pressure. From the results, SAFT and CPA-PR EoS predictions give much better predictions as compare to PR and SRK EoS during zero binary interaction parameters. Meanwhile, SRK and PR EoS can predict well at low pressure. However, SRK and PR EoS performed very bad at high temperature and high pressure (near critical points) as shown in Table 3. In this study, the binary interaction parameters are found to change in the range from -0.25 to 0.3.

Table 4 presents the error analysis of the prediction data using average absolute deviation percentage (AAD%). The predicted data with optimized binary interaction parameters can be summarized as:

- At 304.19 K (SAFT 1.57%>CPA>SRK>PR)
- At 323.15 K (SAFT 1.19%>CPA>PR>SRK)
- At 373.15 K and high pressures (CPA 1.76%>PR>SRK>SAFT)
- At 373.15K and low pressures (SRK 0.6%>PR>CPA>SAFT)
- At 573.15 K (CPA 11.23%>SAFT>SRK >PR)

In terms of graphical presentations, the solubility of CO₂ in water at different temperatures for all selected EoS with optimized binary interaction parameters are plotted in Fig. 1-4 while the solubility of CO₂ in water for individual EoS at different temperatures are plotted in Fig. 5-8 to examine the performance of each EoS. From these figures,

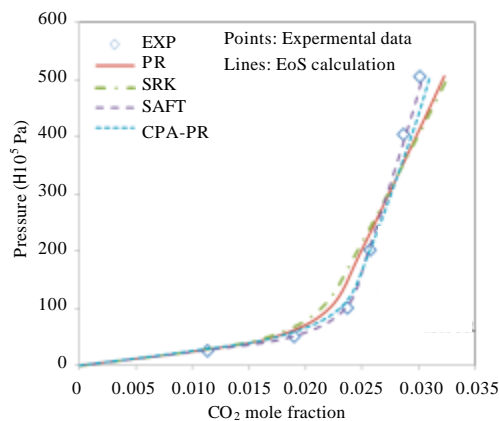


Fig. 1: Solubility of CO₂ in water at 304.19 K

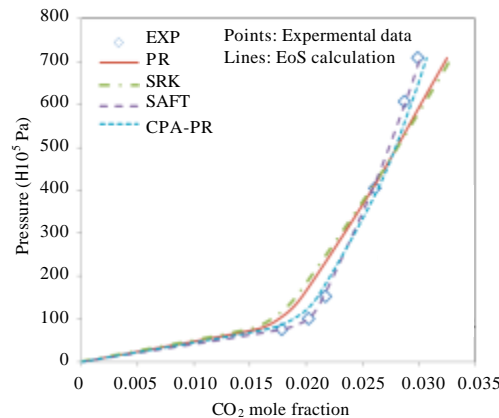


Fig. 2: Solubility of CO₂ in water at 323.15 K

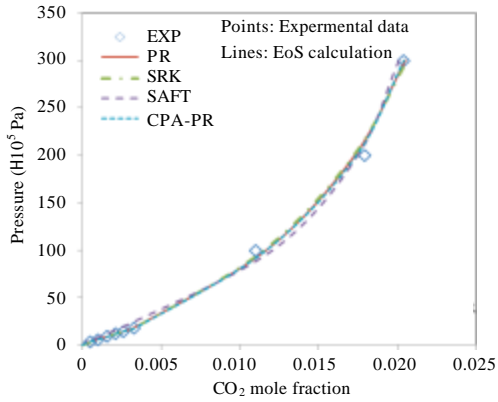


Fig. 3: Solubility of CO₂ in water at 373.15 K

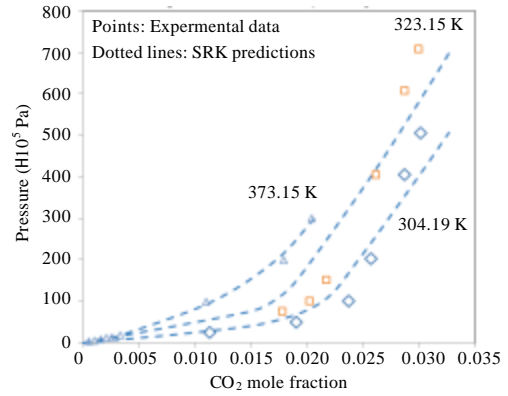


Fig. 6: Solubility of CO₂ in water at different temperatures using optimized binary interaction parameters for SRK prediction

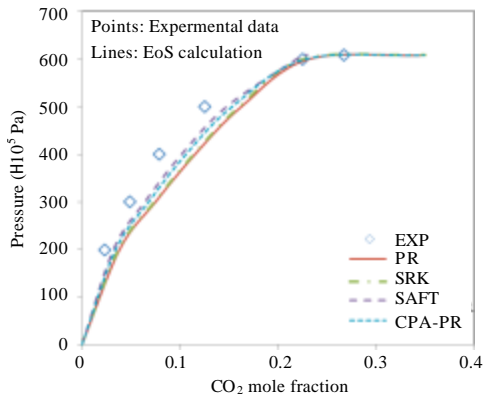


Fig. 4: Solubility of CO₂ in water at 573.15 K

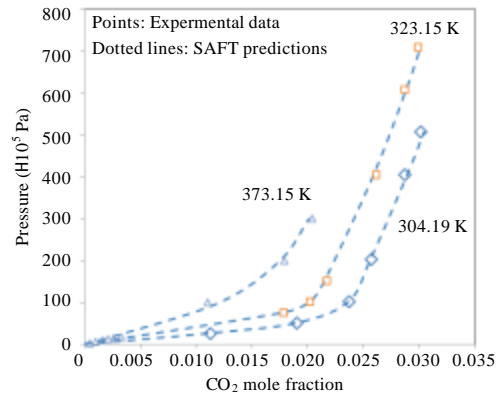


Fig. 7: Solubility of CO₂ in water at different temperatures using optimized binary interaction parameters for SAFT predictions

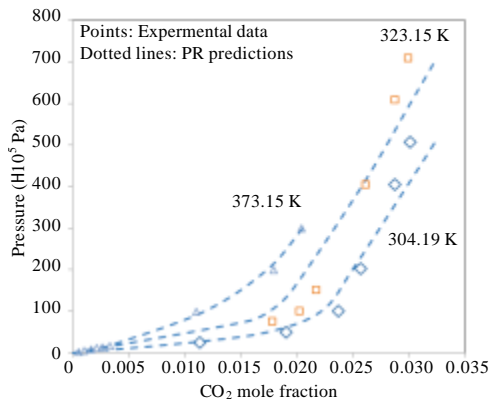


Fig. 5: Solubility of CO₂ in water at different temperatures using optimized binary interaction parameters for PR prediction

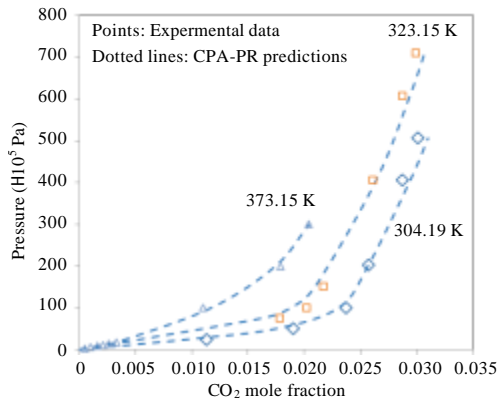


Fig. 8: Solubility of CO₂ in water at different temperatures using optimized binary interaction parameters for CPA-PR predictions

Table 3: Example of EoS prediction data and experimental data phase compositions (mole fraction) for water (H₂O)/carbon dioxide (CO₂) system at 573.15 K. (Todheide and Franke, 1963)

PR										SRK											
Experimental data										$k_{ij} = 0, l_j = 0$		$k_{ij} = 0.0774, l_j = -0.2151$		$k_{ij} = 0.0845, l_j = 0.0375$		$k_{ij} = 0.0627, l_j = -0.2187$		$k_{ij} = 0.0731, l_j = 0.0226$			
Components	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	
										(mol%)											
Pressure = 20 MPa																					
CO ₂	0.352	0.023	0.373	0.043	0.385	0.010	0.381	0.039	0.374	0.039	0.381	0.039	0.374	0.043	0.383	0.011	0.381	0.038	0.381	0.038	
H ₂ O	0.648	0.977	0.627	0.957	0.615	0.991	0.619	0.962	0.626	0.962	0.619	0.962	0.626	0.957	0.618	0.989	0.620	0.620	0.620	0.962	
Pressure = 30 MPa																					
CO ₂	0.454	0.049	0.424	0.088	0.475	0.015	0.446	0.075	0.429	0.075	0.446	0.075	0.429	0.088	0.472	0.018	0.447	0.074	0.447	0.074	
H ₂ O	0.546	0.951	0.577	0.913	0.525	0.985	0.554	0.925	0.571	0.925	0.554	0.925	0.571	0.912	0.529	0.982	0.553	0.553	0.553	0.926	
Pressure = 40 MPa																					
CO ₂	0.480	0.079	0.400	0.144	0.517	0.020	0.448	0.115	0.407	0.115	0.448	0.115	0.407	0.144	0.512	0.023	0.448	0.114	0.448	0.114	
H ₂ O	0.520	0.921	0.600	0.857	0.483	0.981	0.553	0.885	0.593	0.885	0.553	0.885	0.593	0.856	0.488	0.978	0.552	0.552	0.552	0.886	
Pressure = 50 MPa																					
CO ₂	0.460	0.125	*	*	0.545	0.022	0.418	0.163	*	0.163	0.022	0.418	*	*	0.539	0.025	0.418	0.161	0.418	0.161	
H ₂ O	0.540	0.875	*	*	0.455	0.978	0.582	0.837	*	0.837	0.978	0.582	*	*	0.462	0.975	0.582	0.839	0.582	0.839	
Pressure = 60 MPa																					
CO ₂	0.335	0.225	*	*	0.567	0.024	0.357	0.232	*	0.232	0.024	0.357	*	*	0.561	0.027	0.358	0.227	0.358	0.227	
H ₂ O	0.665	0.775	*	*	0.433	0.976	0.643	0.769	*	0.769	0.976	0.643	*	*	0.439	0.973	0.642	0.773	0.642	0.773	
Pressure = 60.8 MPa																					
CO ₂	0.267	0.267	*	*	0.569	0.024	0.240	0.349	*	0.349	0.024	0.240	*	*	0.562	0.027	0.235	0.267	0.235	0.267	
H ₂ O	0.733	0.733	*	*	0.431	0.976	0.760	0.651	*	0.651	0.976	0.760	*	*	0.438	0.973	0.765	0.733	0.765	0.650	
SAFT										CPA-PR											
Experimental data										$k_{ij} = -0.0158, l_j = -0.0220$		$k_{ij} = -0.1094, l_j = 0.0969$		$k_{ij} = -0.0258, l_j = 0.0035$		$k_{ij} = -0.1735, l_j = -0.0344$					
Components	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	*P1	*P2	
										(mol%)											
Pressure = 20 MPa																					
CO ₂	0.352	0.023	0.455	0.020	0.454	0.024	0.448	0.032	0.420	0.032	0.448	0.032	0.420	0.022	0.419	0.025	0.408	0.035	0.408	0.035	
H ₂ O	0.648	0.977	0.545	0.980	0.546	0.976	0.552	0.968	0.580	0.968	0.552	0.968	0.580	0.978	0.581	0.975	0.592	0.966	0.592	0.966	
Pressure = 30 MPa																					
CO ₂	0.454	0.049	0.549	0.037	0.546	0.045	0.525	0.064	0.507	0.064	0.525	0.064	0.507	0.041	0.502	0.046	0.475	0.068	0.475	0.068	
H ₂ O	0.546	0.951	0.451	0.963	0.454	0.955	0.475	0.936	0.493	0.936	0.475	0.936	0.493	0.959	0.498	0.954	0.525	0.932	0.525	0.932	
Pressure = 40 MPa																					
CO ₂	0.480	0.079	0.577	0.052	0.571	0.065	0.521	0.102	0.534	0.102	0.521	0.102	0.534	0.059	0.525	0.068	0.474	0.106	0.474	0.106	
H ₂ O	0.520	0.921	0.424	0.948	0.429	0.936	0.479	0.898	0.466	0.898	0.479	0.898	0.466	0.942	0.475	0.932	0.526	0.894	0.526	0.894	
Pressure = 50 MPa																					
CO ₂	0.460	0.125	0.577	0.067	0.569	0.083	0.469	0.148	0.538	0.148	0.469	0.148	0.538	0.076	0.524	0.089	0.438	0.153	0.438	0.153	
H ₂ O	0.540	0.875	0.423	0.934	0.432	0.917	0.532	0.852	0.462	0.852	0.532	0.852	0.462	0.924	0.476	0.911	0.562	0.847	0.562	0.847	
Pressure = 60 MPa																					
CO ₂	0.335	0.225	0.567	0.080	0.554	0.102	0.369	0.220	0.533	0.220	0.369	0.220	0.533	0.092	0.512	0.111	0.360	0.229	0.360	0.229	
H ₂ O	0.665	0.775	0.433	0.920	0.446	0.899	0.631	0.780	0.467	0.780	0.631	0.780	0.467	0.908	0.488	0.889	0.640	0.772	0.640	0.772	
Pressure = 60.8 MPa																					
CO ₂	0.267	0.267	0.566	0.081	0.553	0.103	0.357	0.230	0.532	0.230	0.357	0.230	0.532	0.094	0.511	0.112	0.239	0.349	0.239	0.349	
H ₂ O	0.733	0.733	0.434	0.919	0.447	0.897	0.643	0.770	0.468	0.770	0.643	0.770	0.468	0.906	0.489	0.888	0.761	0.651	0.761	0.651	

*P1 = phase 1, *P2 = phase 2, ¹Binary interaction parameter from literature (Pfohl *et al.*, 1998), ²Optimized binary interaction parameter, * = Error in calculations

Table 4: Average Absolute Deviation (AAD) between various thermodynamic models at different temperatures using optimized binary interaction parameters

Temperature (K)	Pressure range (bar)	PR			SRK			SAFT			CPA-PR		
		1	2	3	1	2	3	1	2	3	1	2	3
304.19	2533000-50663000	75.519	27.643	8.006	67.489	28.203	7.208	19.670	14.900	1.569	19.563	12.052	3.212
323.15	7599000- 70928000	73.340	27.551	6.015	65.699	27.319	7.104	18.314	13.002	1.194	16.180	10.372	3.581
373.15	10000000-30000000	25.753	27.297	2.058	25.542	27.489	2.234	9.858	2.965	2.760	7.387	3.044	1.763
373.15	325000-1816000	12.474	27.192	1.776	14.104	26.030	0.601	15.348	26.496	9.250	12.702	7.807	2.916
573.15	20000000-60800000	63.066	36.593	13.528	62.882	35.118	13.167	30.631	26.391	12.532	24.558	20.965	11.233

$$\%AAD = \frac{1}{n} \sum_i \left| \frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right| \times 100 \text{ where } x \text{ stands for mol fraction and } n \text{ is the number of experimental data points}$$

it can be seen that the SAFT and CPA EoS prediction lines match closely with the experimental data except for low pressure data at 373.15 K.

CONCLUSION

In this study, two theoretically based EoS, the SAFT and CPA EoS with the consideration of hydrogen bonding effect were used to model the water/carbon dioxide system at both low and high pressures. It was found that SAFT and CPA EoS are in better agreement with experimental data especially at critical region of pure components.

Binary interaction parameters using optimization techniques can greatly enhance the prediction results. However, the optimized binary interaction parameters only work well in the specific sets of data. Both SAFT and CPA EoS can perform satisfactorily for the range of conditions using zero binary interaction parameters.

Although SAFT and CPA EoS represent better the system examined here, the conventional cubic EoS can predict very satisfactorily and even better than SAFT and CPA EoS at low pressures.

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