SHORT COMMUNICATION

UNIQUAC activity coefficient model and modified Redlich- Kwong EOS for the vapor liquid equilibrium systems of carbon dioxide-water

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Abstract

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The UNIQUAC activity coefficient model and fugacity coefficient model of modified Redlich-Kwong predicted vapor-liquid equilibrium between carbon dioxide and water efficiently. The activity coefficient model needed the energy interaction parameters between molecules of carbon dioxide and water. Those parameters can be obtained by non-linear regression method of the experimental data of the vapor-liquid equilibria of carbon dioxide and water (Lide, 1992). The fugacity coefficient model of modified Redlich-Kwong needed only some physical properties of carbon dioxide and water without any interaction parameters. The experimental data had ranges of temperature and partial pressure of carbon dioxide between 10 to 100ºC and 5 to 1,200 kPa, respectively. The parameters for the activity coefficient model are temperature dependent but are not concentration dependent. The regression results gave good agreements with the experimental data in which the mean absolute error (MAE) between experiment and calculated partial pressure of carbon dioxide was 2.72% and the mean absolute standard deviation (MAD) of that error was 1.35%. Comparing the effects of activity coefficients and fugacity coefficients, we found that the non-ideality in vapor phase was more influential than the non-ideality in liquid phase.

Key words : carbon dioxide, UNIQUAC, modified Redlich-Kwong, VLE

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บทคัดย่อ

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แบบจำลองสัมประสิทธิ์แอกติวิตี UNIQUAC และสมการสถานะแบบขยายของ Redlich-Kwong สำหรับสมดุลแก๊ส-ของเหลวของระบบคาร์บอนไดออกไซด์-น้ำ

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แบบจำลองสัมประสิทธิ์แอกติวิตี UNIQUAC และแบบจำลองสัมประสิทธิ์ฟิวกาซิตีแบบขยายของ Redlich-Kwong ให้ผลการทำนายที่ดีต่อระบบสมดุลวัฏภาคแก๊ส-ของเหลวของระบบคาร์บอนไดออกไซด์-น้ำ แบบจำลองสัมประสิทธิ์แอกติวิตี ในบทความนี้ต้องการค่าพารามิเตอร์ของพลังงานอันตรกิริยาระหว่างโมเลกุลของคาร์บอนไดออกไซด์และโมเลกุลของน้ำ การคำนวณค่าพารามิเตอร์ของพลังงานอันตรกิริยาเหล่านั้นจะใช้วิธีการถดถอยไม่เชิงเส้นกับข้อมูลจากการทดลองของสมดุลวัฏภาคของระบบคาร์บอนไดออกไซด์-น้ำ (Lide, 1992) ในขณะที่แบบจำลองสัมประสิทธิ์ฟิวกาซิตีในบทความนี้ ต้องการเฉพาะสมบัติทางกายภาพของแก๊สทั้งสองโดยไม่ต้องการพารามิเตอร์อื่น ๆ จากการทำถดถอย ช่วงของอุณหภูมิและช่วงของความดันของข้อมูลจากการทดลองมีค่าเท่ากับ 10-100°C และ 5-1,200 kPa ตามลำดับ ค่าพลังงานอันตรกิริยาในแบบจำลองสัมประสิทธิ์แอกติวิตีเป็นค่าที่ขึ้นกับอุณหภูมิแต่ไม่ขึ้นกับความเข้มข้น เมื่อนำค่าพารามิเตอร์ที่ได้จากการทำถดถอยไม่เชิงเส้นในการคำนวณค่าความดันย่อยของคาร์บอนไดออกไซด์ ผลปรากฏว่าได้ค่าความคลาดเคลื่อนสัมบูรณ์เฉลี่ย (MAE) ของผลต่างระหว่างความดันย่อยจากการทดลองและจากการคำนวณเท่ากับ 2.72% และค่าเบี่ยงเบนมาตรฐานสัมบูรณ์เฉลี่ยของความคลาดเคลื่อนเท่ากับ 1.35% เมื่อเปรียบเทียบระหว่างค่าของสัมประสิทธิ์แอกติวิตีและค่าสัมประสิทธิ์ฟิวกาซิตีของทั้งระบบ พบว่าระดับของความเบี่ยงเบนไปจากสภาวะอุดมคติของสารละลายในวัฏภาคแก๊สมีค่าสูงกว่าของสารละลายในวัฏภาคของเหลว

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Chemisorption of CO_2 by amine aqueous solutions in gas purification process is very important in petrochemical industries (Kohl and Nielsen, 1997). The process is conducted due to CO_2 reduced heating value of natural gases or may damage downstream industrial plants. Prior to reaching a complicated system of chemisorption, the less sophisticated physisorption systems of CO_2 in water should be investigated. The binary system of CO_2-water was important to study first because the system would give the basic appearance of the solubility of CO_2 in water. Consequently, the complicated model of CO_2 + water + amine system needed the sub-model of CO_2 + water to be accomplished. In this study, we selected UNIQUAC activity coefficient model for the sub-model of the CO_2 + water + amine system. The UNIQUAC model is suitable for these systems since it accounts for the molecular volume and surface area properties of all chemical species in the system.

This study investigated UNIQUAC interaction parameters for the binary system of CO_2-water. Those parameters can be obtained by a non-linear regression method from the experimental data. The parameters were dependent on temperature but were not dependent on concentration. Importantly, the interaction parameters of CO_2 + water systems could be used in the ternary system of CO_2-water-amine without any re-adjustment.

Assumption of the Models

The fluid phase equilibrium system of CO_2 + water was found by equations to be related to partial pressure (P_i) and vapor mole fraction (y_i) as follows:

$$P_1 = \frac{x_1\gamma_1^* H_{12}}{\varphi_1} \qquad P_2 = \frac{x_2\gamma_2 P_2^s}{\varphi_2} \tag{1}$$

$$y_1 = \frac{x_1\gamma_1^* H_{12}}{\varphi_1 P} \qquad y_2 = \frac{x_2\gamma_2 P_2^s}{\varphi_2 P} \tag{2}$$

Note that, according to Dalton's law, the total pressure of the system (P) can be written as: $P = P_1 + P_2$

Where subscripts 1 and 2 refer to CO_2 and water respectively

P_i is a partial pressure of component *i*
γ_i is an activity coefficient of component *i*
φ_i is a fugacity coefficient of component *i*
y_i is a mole fraction in vapor phase of component *i*
x_i is a mole fraction in liquid phase of component *i*
H_{12} is the Henry's constant of solubility of solute 1 in solvent 2
P_2^s is the vapor pressure of water

Superscript * is an unsymmetric convention of activity coefficient. The Henry's constant of CO_2 as a function of temperature and vapor pressure of pure water in water as functions of temperature are shown in Table 1.

Activity coefficients calculated from the UNIQUAC model were developed by excess Gibbs free energy equation (Abrams *et al.*, 1975)

$$\frac{g^E}{RT} = \frac{g^E(\text{Combinatorial})}{RT} + \frac{g^E(\text{Residual})}{RT} \tag{3}$$

where g^E is the excess Gibbs free energy and R is the gas constant. For a binary system, activity coefficients are derived by differentiation of the total excess Gibbs function with respect to mole fraction of different species. The contribution to the activity coefficient of CO_2 was given by unsymmetrical UNIQUAC equation and that of H_2O was given by symmetric UNIQUAC equation (Prausnitz *et al.*, 1999).

In these two cases, the use of a standard state as a pure solvent is often called symmetrical normalization. On the other hand, if the infinite dilution standard state is used for the solute, it is obvious that the unsymmetrical normalization would apply to the solute. Those two normalizations can be expressed as follows:

Symmmetric: $\gamma_i \to 1,\ as \quad x_i \to 1$

Unsymmetric: $\gamma_i \to 1,\ as \quad x_i \to 0$

The unsymmetrical normalization is given by the following:

$$\gamma_1^* = \frac{\gamma_1}{\gamma_1^\infty} \tag{4}$$

where $\gamma_1^\infty = \lim_{x_1 \to 0} \gamma_1$ (5)

Therefore, the activity coefficients of CO_2 and water were obtained as (Sander *et al.*, 1986):

$$\begin{aligned}\ln \gamma_1^{*C} &= \ln \frac{\phi_1}{x_1} - \frac{\phi_1}{x_1} - \ln \frac{r_1}{r_2} + \frac{r_1}{r_2} \\ &\quad - \frac{z}{2} q_1 \left(\ln \frac{\phi_1}{\theta_1} - \frac{\phi_1}{\theta_1} - \ln \frac{r_1 q_2}{r_2 q_1} + \frac{r_1 q_2}{r_2 q_1} \right)\end{aligned} \tag{6}$$

$$\begin{aligned}\ln \gamma_1^{*R} &= q_1(-\ln(\theta_1 + \theta_2 \Psi_{21}) - \frac{\theta_1}{\theta_1 + \theta_2 \Psi_{21}} \\ &\quad - \frac{\theta_2 \Psi_{12}}{\theta_1 \Psi_{12} + \theta_2} + \ln \Psi_{21} + \Psi_{21})\end{aligned} \tag{7}$$

$$\ln \gamma_2^C = \ln \frac{\phi_2}{x_2} + 1 - \frac{\phi_2}{x_2} - \frac{Z}{2} q_2 \left(\ln \frac{\phi_2}{\theta_2} + 1 - \frac{\phi_2}{\theta_2} \right) \tag{8}$$

$$\begin{aligned}\ln \gamma_2^R &= q_2(1 - \ln(\theta_1 \Psi_{12} + \theta_2) - \\ &\quad \frac{\theta_1 \Psi_{21}}{\theta_1 + \theta_2 \Psi_{21}} - \frac{\theta_2}{\theta_1 \Psi_{12} + \theta_2}\end{aligned} \tag{9}$$

where z is coordination number equal to 10. (Prausnitz *et al.*, 1999)

The activity coefficients of the both unsymmetric and symmetric conventions are shown below:

$$\ln \gamma_1^* = \ln \gamma_1^{*C} + \ln \gamma_1^{*R} \tag{10}$$

$$\ln \gamma_2 = \ln \gamma_2^C + \ln \gamma_2^R \tag{11}$$

Table 1. Henry's constant of CO_2 in water (H_{12}) and vapor pressure of water (P_2^s)

	Expression	Range	Source
H_{12}	$\ln H_{12} = 192.876 - \frac{9624.41}{T} - 28.7488\ln(T) + 1.44074\times10^{-2}T$	273-473 K	Kamps *et al.*, 2001
P_2^s	$\ln P_2^s = 72.55 - 7206.7T - 7.1385\ln(T) + 4.04\times10^{-6}T^2$	273-650 K	Posey and Rochelle, 1997

Other variables used in UNIQUAC equations can be written as:

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \tag{12}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \tag{13}$$

where r_i and q_i are volume parameters and surface area parameters of pure components (Bondi, 1968). In this research r_i and q_i were evaluated from van der Waals group parameters and are shown in Table 2 as follows:

Interaction energy parameters Ψ_{12} and Ψ_{21} related to internal energy, u_{ij}, were estimated by non-linear regression method. The relationship between these parameters and internal energies were shown as follows:

$$\Psi_{12} = \exp\left(-\frac{u_{12} - u_{22}}{RT}\right) = \exp\left(-\frac{\tau_{12}}{RT}\right) \tag{14}$$

$$\Psi_{21} = \exp\left(-\frac{u_{21} - u_{11}}{RT}\right) = \exp\left(-\frac{\tau_{21}}{RT}\right) \tag{15}$$

Where R is equal to 8.31451 $J\cdot mol^{-1}\cdot K^{-1}$. According to equations 14 and 15, it is obvious that $\Psi_{11} = \Psi_{22} = 1.0$. In this work, the parameters τ_{12} and τ_{21} were set to be dependent on temperature. Therefore, τ_{12} and τ_{21} were related to temperature by means of independent parameters (β_i's) as follows:

$$\tau_{12} = \beta_1 + \frac{\beta_2}{T} \tag{16}$$

$$\tau_{21} = \beta_3 + \frac{\beta_4}{T} \tag{17}$$

Besides activity coefficient calculation, we can estimate fugacity coefficients of CO_2 and water in vapor phase. Since the systems were not agreeable with ideal gas behavior, the fugacities were required to represent the gas behavior. Fugacity coefficient model in this work was presented by the modified Redich-Kwong Equation of State (Soave, 1972):

$$P = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)} \tag{18}$$

Then fugacity coefficients were calculated by:

$$\ln \varphi_i = \int_{\infty}^{v}\left[\frac{1}{v} - \frac{1}{RT}\left[\frac{dP}{dn_i}\right]_{T,P,n_j}\right]dv - \ln Z_e \tag{19}$$

Table 2. Volume parameters (r_i), surface area parameters (q_i) and molecular weight of CO_2 and water. (Abrams *et al.*, 1975)

Component	r_i	q_i	MW.
CO_2 (1)	1.3	1.12	44
H_2O (2)	0.92	1.40	18

Table 3. Critical temperatures (T_{ci}), critical pressures (P_{ci}) and dimentionless factors (α_i) of CO_2 and water. (Prausnitz *et al.*, 1999)

Component	T_{ci} (K)	P_{ci} (bar)	α_i
CO_2 (1)	304.1	73.8	1.30
H_2O (2)	647.3	221.2	1.354

$$\ln \varphi_i = \frac{b_i}{b}(z_e - 1) - \ln\,(z_e - B)$$

$$-\frac{\mathrm{A}}{\mathrm{B}}\left(2\frac{a_i^{0.5}}{a^{0.5}} - \frac{b_i}{b}\right)\ln\left(1 + \frac{\mathrm{B}}{\mathrm{Z_e}}\right) \quad (20)$$

Many variables to calculate fugacity coefficients in equation (20) were obtained by:

$$A = 0.42747\frac{P}{T^2}\sum_{i=1}^{n}\left(y_i\frac{T_{ci}\alpha_i^{0.5}}{P_{ci}^{0.5}}\right)^2 \quad (21)$$

$$B = 0.08664\frac{P}{T}\sum_{i=1}^{n} y_i\frac{T_{ci}}{P_{ci}} \quad (22)$$

$$\frac{a_i^{0.5}}{a^{0.5}} = \frac{\alpha_i^{0.5}T_{ci}/P_{ci}^{0.5}}{\sum_{i=1}^{n} y_i\alpha_i^{0.5}T_{ci}/P_{ci}^{0.5}} \quad (23)$$

$$\frac{b_i}{b} = \frac{T_{ci}/P_{ci}}{\sum_{i=1}^{n} y_i\,T_{ci}/P_{ci}} \quad (24)$$

The compressibility factor (z_e), used in equation (20) and (21), was obtained by solving in one of three real roots in equation (25). The largest root of equation (25) was the solution of z_e.

$$Z_e^3 - Z_e^2 + Z_e(A - B - B^2) - AB = 0 \quad (25)$$

The specific properties of each component are critical temperature (T_{ci}), critical pressure (P_{ci}) and dimensionless factor (α_i) that were shown in Table 3.

Estimation of Parameters

The experimental data CO_2-water system (Lide, 1992) were the relationship between partial pressure and concentration of CO_2 at the temperature ranges of 10 to 100ºC. The total number of data was 90.

The evaluation of parameters τ_{12} and τ_{21} in equation (16) and (17) were obtained by non-linear regression method that was set mole fraction as independent variable and partial pressure as dependent variable. The regression used least square method to obtain τ_{12} and τ_{21} by the following equation:

$$Least\ Square = \sum_{i=1}^{n}\left(x_i^{cal} - x_i^{exp}\right)^2 + \sum_{i=1}^{n}\left(P_i^{cal} - P_i^{exp}\right)^2 \quad (26)$$

where *i* was a data number, *x* was mole fraction of CO_2 in liquid phase, *n* was the total number of data, P_i was partial pressure of CO_2, superscript, *cal* was mole fraction or partial pressure of CO_2 from calculation and superscript, *exp* was mole fraction or partial pressure of CO_2 from experiments. Least square calculation can be used by Fortran 77 with subroutine ODRPACK (Boggs *et al.*, 1992a,b) to determine β_1, β_2, β_3 and β_4 in equation (16) and (17) respectively. The simulation flow chart is illustrated in Figure 1.

Calculation Results and Discussion

The regression results of independent parameters β_1, β_2, β_3 and β_4 in equation (16) and (17) can be written again as:

$$\tau_{12} = \beta_1 + \frac{\beta_2}{T} \quad \text{and} \quad \tau_{21} = \beta_3 + \frac{\beta_4}{T}$$

The obtained values of β_1, β_2, β_3 and β_4 are listed as follows (Katawut, 2002):

β_1 = 708.96173 *J/mol*, β_2 = 319.76499×10^3 *J·K/mol*

β_3 = -4597.4706 *J/mol*, β_4 = 1670.9929×10^3 *J·K/mol*

Substituting β_1, β_2, β_3 and β_4 into the UNIQUAC equation, one would obtain activity coefficients of all species in the systems. The calculation of mean absolute error (MAE) for all experimental data of carbon dioxide partial pressure and mean absolute standard deviation of the errors (MAD) gave 2.72% and 1.35% respectively. Appendix 1 and Appendix 2 show the comparison of partial vapor pressure of CO_2 obtained from the model with their experimental values. Furthermore, Appendix 1 also illustrates the calculation results of activity and fugacity coefficients.

Use of the model is widely applicable due to the wide ranges of temperature and pressure. The model should apply the whole system of CO_2 aqueous solutions. Moreover, the model should be a good basis for the other systems of solubilities of CO_2 such as the solubilities of CO_2 in sucrose solutions, the solubilities of CO_2 in beverage industries and the solubilities of CO_2 in scrubbers

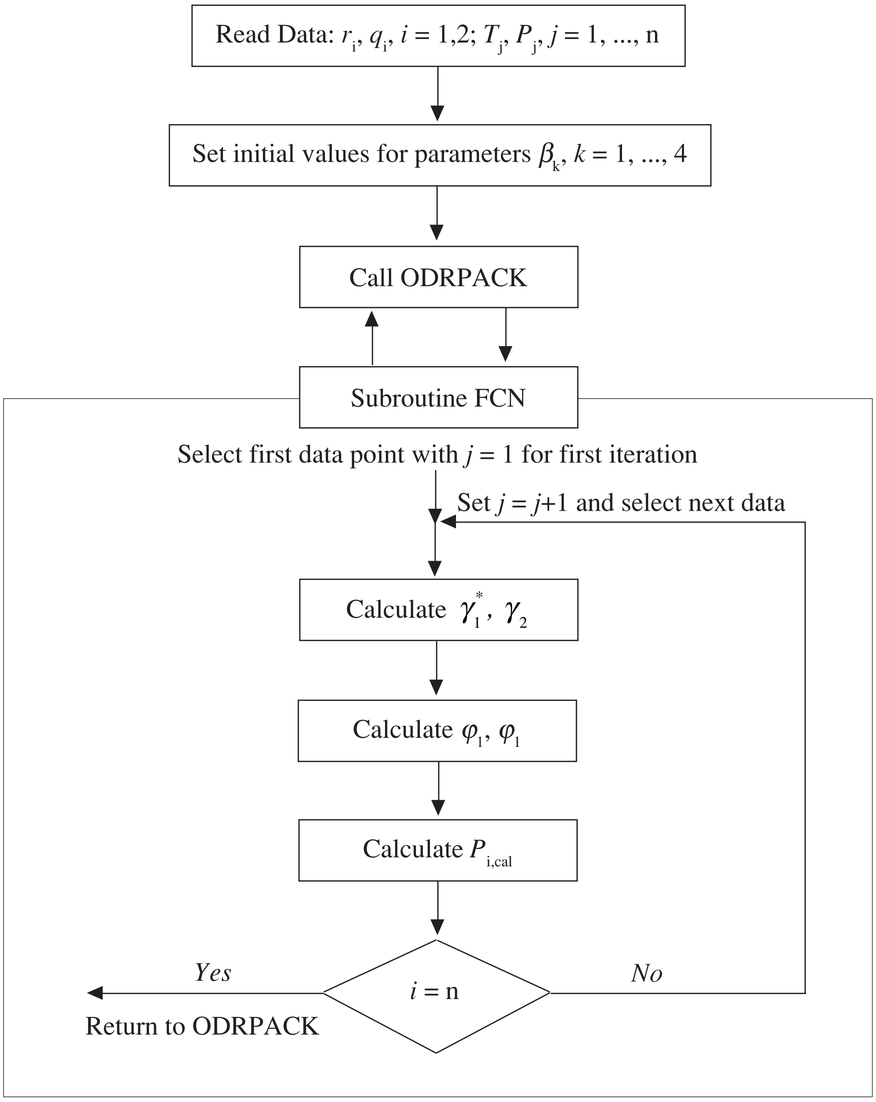

Figure 1. Flow chart of the non-linear regression to determine the energy interaction parameters (β_k).

of natural gas plants.

Conclusions

The use of UNIQUAC activity coefficient model and the modified Redlich-Kwong EOS can predict the VLE system of CO_2 aqueous solutions satisfactorily. The calculation was applied to wide ranges of temperature and CO_2 pressure. The experimental data were obtained from the well-known chemical engineers' handbook (Lide, 1992) whereas the shape and size parameters of the UNIQUAC model were obtained from the original work of the model (Abrams and Prausnize, 1975). The non-linear regression subroutine, ODRPACK, to obtain energy interaction parameters was well-known free software from the National Institute of Standards and Technology (Boggs *et al.*, 1992a,b). The use of the activity coefficient model and fugacity coefficient model provided satisfactory low mean absolute error and low mean absolute deviation of CO_2 partial pressure from the experimental data. Future work related to these results should address other systems of CO_2 solubilities which are based on aqueous solutions such as in the beverage industry or in electrolyte solutions.

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Appendix 1.

Aqueous solubility data of carbon dioxide at various temperatures (Lide, 1992) including the calculation results of activity coefficients, fugacity coefficients and CO_2 partial vapor pressures.

Data #	T (K)	x_{co_2}	γ_{H_2O}	γ_{co_2}	φ_{H_2O}	φ_{co_2}	P_{exp} (kPa)	P_{cal} (kPa)
1	283.15	4.80e-05	0.999784	1.000000	0.999533	0.999216	5	5.11
2	283.15	9.60e-05	0.999569	1.000000	0.999152	0.998592	10	10.22
3	283.15	1.91e-04	0.999142	1.000000	0.998401	0.997355	20	20.35
4	283.15	2.87e-04	0.998711	1.000000	0.997641	0.996106	30	30.60
5	283.15	3.82e-04	0.998285	1.000000	0.996889	0.994869	40	40.76
6	283.15	4.77e-04	0.99786	1.000000	0.996137	0.993632	50	50.93
7	283.15	9.50e-04	0.995743	1.000002	0.992385	0.987466	100	101.75
8	283.15	0.001	0.99552	1.000002	0.991988	0.986814	100.97	107.15
9	283.15	0.0019	0.99151	1.000008	0.984821	0.975045	201.07	204.86
10	283.15	0.0038	0.983111	1.000032	0.969564	0.95004	398.81	415.37
11	283.15	0.0056	0.975238	1.000070	0.954931	0.92611	592.52	620.54
12	283.15	0.0072	0.968308	1.000116	0.941754	0.904601	782.11	808.06
13	283.15	0.0088	0.96144	1.000174	0.928394	0.882826	967.02	1000.90
14	288.15	4.10e-05	0.999823	1.000000	0.999517	0.999183	5	5.11
15	288.15	8.20e-05	0.999646	1.000000	0.99915	0.99858	10	10.23
16	288.15	1.64e-04	0.999291	1.000000	0.998418	0.997373	20	20.48
17	288.15	2.45e-04	0.998941	1.000000	0.997694	0.996182	30	30.61
18	288.15	3.27e-04	0.998587	1.000000	0.996961	0.994975	40	40.89
19	288.15	4.09e-04	0.998233	1.000000	0.996228	0.993767	50	51.17
20	288.15	8.14e-04	0.996487	1.000002	0.992601	0.987795	100	102.17
21	288.15	0.001	0.995686	1.000002	0.990932	0.985048	119.67	125.70
22	288.15	0.002	0.991396	1.000009	0.981915	0.970222	239.37	253.43
23	288.15	0.0039	0.98331	1.000033	0.964574	0.941768	479.05	502.15
24	288.15	0.0057	0.975728	1.000070	0.947856	0.914405	717.35	745.76
25	288.15	0.0074	0.968635	1.000118	0.931768	0.888122	954.84	983.81
26	288.15	0.0091	0.961609	1.000179	0.915339	0.861324	1189.77	1230.54
27	293.15	3.50e-05	0.999823	1.000000	0.999517	0.999183	5	5.06
28	293.15	7.10e-05	0.999646	1.000000	0.99915	0.99858	10	10.27
29	293.15	1.41e-04	0.999291	1.000000	0.998418	0.997373	20	20.40
30	293.15	2.12e-04	0.998941	1.000000	0.997694	0.996182	30	30.69
31	293.15	2.83e-04	0.998587	1.000000	0.996961	0.994975	40	40.99
32	293.15	3.53e-04	0.998233	1.000000	0.996228	0.993767	50	51.16
33	293.15	0.0007	0.997082	1.000001	0.992853	0.988183	97.26	101.77
34	293.15	7.04e-04	0.996487	1.000002	0.992601	0.987795	100	102.36
35	293.15	0.0014	0.994176	1.000004	0.985817	0.976589	194.39	204.85
36	293.15	0.0027	0.988807	1.000015	0.972616	0.95487	387.06	399.90
37	293.15	0.004	0.983475	1.000033	0.959221	0.932877	579.57	600.00
38	293.15	0.0052	0.978586	1.000057	0.946666	0.912299	711.7	789.60
39	293.15	0.0064	0.973729	1.000085	0.933905	0.891415	960.1	984.29
40	298.15	3.10e-05	0.999875	1.000000	0.999457	0.999065	5	5.14
41	298.15	6.20e-05	0.99975	1.000000	0.999113	0.998499	10	10.27
42	298.15	1.23e-04	0.999503	1.000000	0.99844	0.997388	20	20.40
43	298.15	1.85e-04	0.999253	1.000000	0.997757	0.996258	30	30.69

Data #	T **(K)**	x_{co_2}	γ_{H_2O}	γ_{co_2}	φ_{H_2O}	φ_{co_2}	P_{exp} **(kPa)**	P_{cal} **(kPa)**
44	298.15	2.47e-04	0.999003	1.000000	0.997073	0.995128	40	41.01
45	298.15	3.08e-04	0.998756	1.000000	0.9964	0.994016	50	51.17
46	298.15	0.0006	0.997579	1.000001	0.993173	0.988684	98.5	99.96
47	298.15	6.14e-04	0.997523	1.000001	0.993018	0.988428	100	102.31
48	298.15	0.0012	0.995167	1.000003	0.986508	0.977679	196.77	201.15
49	298.15	0.0024	0.990363	1.000011	0.973026	0.955459	394.57	407.38
50	298.15	0.0035	0.985987	1.000025	0.960477	0.934815	590.1	601.25
51	298.15	0.0046	0.981635	1.000043	0.947723	0.913872	787.18	800.14
52	298.15	0.0057	0.977308	1.000066	0.934744	0.892589	984	1004.47
53	308.15	2.40e-05	0.999909	1.000000	0.999355	0.998866	5	5.07
54	308.15	4.80e-05	0.999817	1.000000	0.999037	0.998342	10	10.15
55	308.15	9.70e-05	0.999631	1.000000	0.998393	0.997276	20	20.51
56	308.15	1.45e-04	0.999448	1.000000	0.997764	0.996233	30	30.68
57	308.15	1.93e-04	0.999266	1.000000	0.997135	0.99519	40	40.86
58	308.15	2.42e-04	0.999079	1.000000	0.996493	0.994126	50	51.27
59	308.15	0.0005	0.998099	1.000000	0.993105	0.988509	98.91	106.26
60	308.15	4.81e-04	0.998171	1.000001	0.993355	0.988924	100	102.20
61	308.15	0.0009	0.996581	1.000001	0.987828	0.979764	198.28	192.21
62	308.15	0.0019	0.9928	1.000007	0.97448	0.957682	397.18	410.91
63	308.15	0.0028	0.989414	1.000015	0.962265	0.937512	597.79	612.73
64	308.15	0.0037	0.986042	1.000026	0.949839	0.917027	798.1	819.66
65	308.15	0.0045	0.983058	1.000039	0.938598	0.898523	998.48	1008.23
66	348.15	1.20e-05	0.999962	1.000000	0.998072	0.996377	5	4.89
67	348.15	2.50e-05	0.99992	1.000000	0.997808	0.995941	10	10.20
68	348.15	4.90e-05	0.999844	1.000000	0.997325	0.995141	20	19.99
69	348.15	7.40e-05	0.999764	1.000000	0.996828	0.994314	30	30.21
70	348.15	9.90e-05	0.999683	1.000000	0.996334	0.99349	40	40.43
71	348.15	1.23e-04	0.999607	1.000000	0.995862	0.992701	50	50.26
72	348.15	2.45e-04	0.999218	1.000000	0.993475	0.988699	100	100.33
73	348.15	0.0005	0.998405	1.000000	0.98849	0.980325	211.08	205.74
74	348.15	0.001	0.996813	1.000002	0.978634	0.963774	422.54	415.42
75	348.15	0.0015	0.995224	1.000003	0.968639	0.94701	633.7	629.27
76	348.15	0.0019	0.993956	1.000006	0.960533	0.933428	845.88	803.52
77	348.15	0.0024	0.992374	1.000009	0.950252	0.916221	1058.17	1025.53
78	373.15	1.00e-05	0.99997	1.000000	0.99599	0.992292	5	5.08
79	373.15	2.00e-05	0.999941	1.000000	0.995769	0.991926	10	10.17
80	373.15	3.90e-05	0.999885	1.000000	0.995352	0.991234	20	19.84
81	373.15	5.90e-05	0.999825	1.000000	0.994917	0.990508	30	30.03
82	373.15	7.90e-05	0.999766	1.000000	0.994484	0.989786	40	40.22
83	373.15	9.80e-05	0.99971	1.000000	0.994075	0.989101	50	49.92
84	373.15	1.96e-04	0.99942	1.000000	0.991985	0.985587	100	100.04
85	373.15	0.0002	0.999408	1.000000	0.9919	0.985444	102.37	102.09
86	373.15	0.0004	0.998816	1.000000	0.987673	0.978302	204.45	205.01
87	373.15	0.0007	0.99793	1.000001	0.981331	0.967561	408.86	360.98
88	373.15	0.0011	0.99675	1.000002	0.972809	0.953124	614.31	572.01
89	373.15	0.0015	0.995571	1.000003	0.964186	0.938523	820.92	786.71
90	373.15	0.0018	0.994689	1.000005	0.957644	0.927455	1028.75	950.25

Appendix 2.

Comparison of model predictions with experimental data of CO_2 partial pressures at various temperatures of water-CO_2 system