

Progress in the Study on the Phase Equilibria of the CO₂-H₂O and CO₂-H₂O-NaCl Systems*

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Abstract To study the feasibility of CO₂ geological sequestration, it is needed to understand the complicated multiple-phase equilibrium and the densities of aqueous solution with CO₂ and multi-ions under wide geological conditions (273.15—473.15K, 0—60MPa), which are also essential for designing separation equipments in chemical or oil-related industries. For this purpose, studies on the relevant phase equilibria and densities are reviewed and analyzed and the method to improve or modify the existing model is suggested in order to obtain more reliable predictions in a wide temperature and pressure range. Besides, three different models (the electrolyte non random two-liquid (ELECRTL), the electrolyte NRTL combining with Helgeson model (ENRTL-HG), Pitzer activity coefficient model combining with Helgeson model (PITZ-HG)) are used to calculate the vapor-liquid phase equilibrium of CO₂-H₂O and CO₂-H₂O-NaCl systems. For CO₂-H₂O system, the calculation results agree with the experimental data very well at low and medium pressure (0—20MPa), but there are great discrepancies above 20MPa. For the water content at 473.15K, the calculated results agree with the experimental data quite well. For the CO₂-H₂O-NaCl system, the PITZ-HG model show better results than ELECRTL and ENRTL-HG models at the NaCl concentration of 0.52mol·L⁻¹. But for the NaCl concentration of 3.997mol·L⁻¹, using the ELECRTL and ENRTL-HG models gives better results than using the PITZ-HG model. It is shown that available experimental data and the thermodynamic calculations can satisfy the needs of the calculation of the sequestration capacity in the temperature and pressure range for disposal of CO₂ in deep saline aquifers. More experimental data and more accurate thermodynamic calculations are needed in high temperature and pressure ranges (above 398.15K and 31.5MPa).

Keywords CO₂-H₂O, CO₂-H₂O-NaCl, high temperature high pressure, phase equilibrium, density

1 INTRODUCTION

The concentration of CO₂ in atmosphere has increased greatly because of the fossil fuel (such as natural gas, petroleum, and coal) combustion, which leads to a significant climate warming and weather changes. In 1997, the Kyoto Protocol clearly states the reduction of greenhouse gases emissions[1]. Since CO₂ is believed to be one of the most important greenhouse gases being responsible for about 64% of the enhanced “greenhouse effect”[2], the disposal of CO₂ has become an issue of worldwide concern.

Geological sequestration, generally referred to the injection of carbon dioxide into deep saline aquifers, depleted hydrocarbon reservoirs, or deep coalbeds, is currently attracting attention[3] because of the large capacity and long residence time. It is believed that environmental consequence of such an approach would be broadly neutral[4].

In order to predict the sequestration potential and to study the long-term behavior of carbon dioxide in the geologic reservoirs, it is needed to study the complicated multiple-phase equilibrium and the densities of the aqueous solution containing CO₂ and ions (Na⁺, K⁺, Mg²⁺, Ca²⁺ and Cl⁻ etc.) under the geological conditions with wide temperature and pressure range. Since the phase behavior of the CO₂-H₂O-ions system is complicated, and Na⁺ and Cl⁻ are the main components, it is usually simplified to study the phase

equilibrium for the CO₂-H₂O and CO₂-H₂O-NaCl systems. In addition, it is necessary to study the phase equilibrium in order to simulate the CO₂-related enhanced oil recovery processes and to design separation equipments in the chemical or oil-related industries such as the extraction with supercritical carbon dioxide and the removal of the acid gases as carbon dioxide.

For this purpose, the phase equilibrium and the densities of the CO₂-H₂O and CO₂-H₂O-NaCl systems in a wide temperature and pressure range (273.15—473.15K, 0—60MPa) are reviewed. Experimental data and thermodynamic models are also evaluated, and the existing problems and research direction are put forward, to provide a basis for further study of these two systems and a reference for the study of other gas-electrolyte aqueous solutions. Besides, three different models have been used to calculate the vapor-liquid phase equilibrium of CO₂-H₂O and CO₂-H₂O-NaCl systems and the calculation results are compared with the experimental data.

2 EXPERIMENTAL STUDIES ON THE PHASE EQUILIBRIUM OF CO₂-H₂O AND CO₂-H₂O-NaCl SYSTEMS.

2.1 CO₂-H₂O system

CO₂ solubility in aqueous solution and the density of aqueous CO₂ solutions at different temperatures and

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pressures are required for modeling CO₂ geological sequestration and migration in reservoirs[5].

Diamond and Akinfiyev[6] evaluated 520 experimental data from 25 references on the CO₂ solubility in pure water under from 271.65 to 373.15K and from 0.1 to 100MPa, and 158 data were discarded. Spycher *et al.* reviewed the mutual solubilities of CO₂ and H₂O in the range of 285.15—373.15K and 0—60MPa[3]. Chapoy *et al.* reviewed reliable experimental data for CO₂ solubility in water and water content in the CO₂-H₂O system at 273.15—373.15K and 0.07—70.9MPa[7]. This paper reviews more extensive experimental data for CO₂ solubility in water and water content for the CO₂-H₂O system in a wider range of temperature and pressure (0—473.15K, 0.07—70.9MPa). The available experimental data are summarized in Table 1.

From the survey results listed in Table 1, it is known that the mutual solubilities of CO₂ and H₂O

measured at high temperature and pressure are scarce. This is because of the rigorous requirement on the experimental equipment at high temperature and pressure and the high cost of manpower and material resources to carry out the experiment.

Disposal of CO₂ in deep saline aquifers is considered to be, by far, the largest potential capacity, of the order of 1×10^{12} [36], and its application needs the understanding of CO₂ solubility in water at the temperature and pressure of 303.15—333.15K, 10—20MPa. In order to see the consistency of experimental data from different sources, Fig.1 shows the distribution of the available experimental data at the temperature of 323.15K.

Figure 1 shows the inconsistency of the experimental data from different sources, which implies the necessity to evaluate the available experimental data. Fig.1(b) shows the comparison of the experimental data from different sources with great discrepancies

Table 1 Summary of experimental data for the mutual solubilities of carbon dioxide and water^①

T, K	P, MPa	Number of the experimental data	Type	Ref.	Year
291.15—373.15	2.53—70.9	50	x	[8,9]	1939,1940
298.15—348.15	0.10—70.93	39	y	[10]	1941
283.15—303.15	0.101—2.027	15	x	[11]	1956
323.15,373.15	20,50	4(x), 4(y)	x & y	[12]	1963
383.15—473.15	10—70	7(x), 7(y)	x & y	[13]	1964
303.15—353.15	0.993—3.891	13	x	[14]	1969
298.15—373.15	1.733—5.147	22	y	[15]	1971
298.15—348.15	4.955	5	x	[16]	1972
298.15, 373.15	4.955	5	x	[17]	1975
323.15—473.15	0.154—5.389	33	x	[18]	1981
323.15	6.82—17.68	8 (x), 7(y)	x & y	[19]	1987
298.15	3.63	1	y	[20]	1987
285.15—304.21	0.69—13.79	19	y	[21]	1987
323.15,348.15	10.133,15.20	4(x), 4(y)	x & y	[22]	1988
373.15—473.15	0.325—8.0	49(x), 49(y)	x & y	[23]	1988
353.35—471.25	2.040—10.210	33	x	[24]	1989
348.15	10.34—20.94	2(x), 3(y)	x & y	[25]	1991
288.15—313.15	5.17—24.3	37(x), 41(y)	x & y	[26]	1992
323.15	10.1—30.1	3(x), 3(y)	x & y	[27]	1993
323.15, 348.15	34.48	2	y	[28]	1995
304.19, 313.15	1.712—5.825	10	x	[29]	1998
298.31—298.57	2.7—5.33	7	x	[30]	2000
323.15—353.15	4.05—14.11	29(x), 29(y)	x & y	[31]	2000
274.15—288.15	0.07—2.179	54	x	[32]	2002
313.20—393.17	0.00718—9.2576	43	x	[33]	2002
303.15—333.15	10—20	12	x	[34]	2003
274.14—351.31	0.190—9.333	27	x	[7]	2004
278.22—318.23	0.464—7.963	47(x), 30(y)	x & y	[35]	2004
332.15	3.34—19.89	6	x	[5]	2004

① x: carbon dioxide solubility in water; y: water content in CO₂-rich phase.

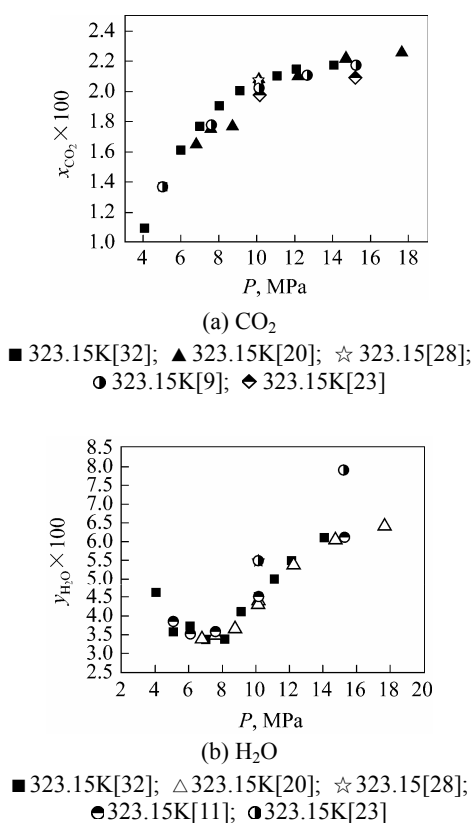


Figure 1 Experimental data for the mutual solubilities of carbon dioxide and water

for part of them. From Fig.1(b) it is found that the experimental water content data in the CO₂-rich phase decreases first and then increases with increasing pressure.

Meanwhile, compared to the solubility of CO₂ in water, the water content in CO₂-rich phase shown in Fig.1 is lower by a factor of 0.1. This is due to the property difference of molecular carbon dioxide and water. Carbon dioxide is a non-polar molecule and the intermolecular force is the London force. While water is a strong polar molecule and intermolecular interaction depends primarily on hydrogen bonds. In the CO₂-H₂O binary mixture, molecular interactions be-

tween two like molecules are much stronger than those between two unlike molecules (H₂O and CO₂). This dissimilarity results in the low solubility of H₂O in the CO₂-rich phase. The electrostatic forces of water molecules can polarize CO₂ molecules, then increase their ability to penetrate the water phase, consequently, the solubility of CO₂ in water is much larger than that of water in CO₂[37].

Table 2 shows the summary of the experimental density in the CO₂-rich phase and H₂O-rich phase with saturated or unsaturated CO₂, respectively. Most of the experimental densities of the CO₂-H₂O system are measured at low pressures (<20MPa), and it is necessary to determine the density experimentally at high pressure.

2.2 CO₂-H₂O-NaCl system

Na⁺ and Cl⁻ are the main components in natural water[42], and it is a must to study not only the CO₂-H₂O system, but also the effect of ions on the properties of this solution. Therefore, the CO₂ solubility in aqueous NaCl solutions is surveyed, and the available experimental data are summarized in Table 3.

As shown in Table 3, the experimental data measured at pressures higher than 20 MPa are quite scarce in the whole temperature range. It is crucial to accumulate experimental data on the CO₂ solubilities in aqueous NaCl solutions at high temperature and pressure.

Experimental densities for the CO₂-H₂O-NaCl system are only measured by Nighswander *et al.*[24] at low NaCl concentrations (1%, by mass) at the temperature of 353.35—471.25K and pressure of 2.040—10.210MPa. The density decreases with increasing temperature, but the effect of pressure on the density is unobvious.

As is described in Ref.[3], the typical equilibrium subsurface conditions is based on a mean surface temperature of 293.15K, a geothermal gradient of 35K·km⁻¹, and a hydrostatic pressure gradient of 10.5MPa·km⁻¹. For the temperature and pressure range of disposal of CO₂ in deep saline aquifers, available experimental data can nearly satisfy the needs of the calculation for the sequestration capacity, but the reliability of the

Table 2 Summary of the experimental densities of the CO₂-H₂O system

	<i>T</i> , K	<i>P</i> , MPa	Number of the experimental data	Ref.	Year
saturated CO ₂ -H ₂ O	353.35—471.25	2.040—10.210	33	[24]	1989
	288.1—298.1	6—24	27	[26]	1992
	278—293	6.44—29.49	24	[38]	1997
	304.1	1.0—10.0	14	[37]	2000
	294—374	0—30	38	[39]	2000
	332.15	3.34—28.59	29	[5]	2004
	283.80—333.23	1.09—30.66	164	[40]	2004
H ₂ O-rich	332.15	3.34—28.59	29	[5]	2004
CO ₂ -rich	373.15—473.15	0.208—3.350	142	[18]	1981
	323.15—498.15	0.0855—10.2367	297	[41]	1988

Table 3 Summary of the experimental data for CO₂ solubility in aqueous NaCl solutions

T, K	P, MPa	Number of the experimental data	Ref.	Year
273—313	0.102—0.109	18	[43]	1941
273—323	0.102—0.114	66	[44]	1943
445—610	2.5—20.0	54	[45]	1963
423—723	10—140	123	[46]	1965
298—348	4.79	16	[47]	1972
298—423	4.79	16	[48]	1975
288.15—308.15	0.1013	27	[49]	1979
353.15—473.65	2.110—10.030	34	[24]	1989
313—433	0.1—10	63	[50]	1994
303.15—323.15	1.773—5.896	60	[29]	1998
313.31—353.08	0.00643—10.100	70	[33]	2002
303.15—333.15	10—20	36	[34]	2003

data from different sources should be further validated. Considering the injection of carbon dioxide into depleted hydrocarbon reservoirs, sometimes the depth of the abandoned oil and gas reservoirs reaches more than 3000m, which corresponds to a temperature of 398.15K, a pressure of 31.5MPa. The available experimental data at such high temperature and pressure are very scarce and more data at high temperatures and pressures should be reported.

3 THERMODYNAMIC MODELING

3.1 Review of the thermodynamic models

3.1.1 CO₂-H₂O system

Many models, based on the activity coefficient (γ)-fugacity coefficients (ϕ) or ϕ - ϕ approach, have been proposed to calculate the phase equilibria and density for the CO₂-H₂O system. In the γ - ϕ approach, an equation of state (EOS) is used to describe the non-ideality of the CO₂-rich phase and Henry's law or an excess molar Gibbs free energy (G^E) model is used to describe the non-ideality of the H₂O-rich phase. While in the ϕ - ϕ approach, an EOS is used to describe the non-ideality of both phases[51].

Phase equilibrium of the CO₂-H₂O system has been studied extensively by the γ - ϕ approach. The EOS used may be Krichevsky-Kasarnovsky (KK) EOS, Peng-Robinson (PR) EOS and its modifications, Redlich-Kwong (RK) EOS and its modifications, Patel-Teja (PT) EOS, and so on.

Carroll and Mather[52] studied phase equilibria of the CO₂-H₂O system by the KK equation which is reliable at temperatures lower than 373.15K. Kiepe *et al.*[33] calculated gas solubilities (isothermal P - x data) for the CO₂-H₂O system at the temperature and pressure of 313—393K and 0—10MPa by coupling the predictive Soave-Redlich-Kwong (PSRK) group contribution EOS with the model of LIFAC, and the prediction is in good agreement with the experimental data. Valtz *et al.*[35] calculated vapour-liquid equilibrium (VLE) of the CO₂-H₂O system at the temperature and pressure of 278.2—318.2K and 0.464—7.963MPa

by using a thermodynamic model. This model was based upon a dissymmetric approach, in which PR EOS with classical mixing rules was used for the vapour phase, and the aqueous phase followed Henry's law. The prediction of this model showed that the CO₂ solubility is in good agreement with experimental data, but there are discrepancies for the water content in the CO₂-rich phase. Moreover, the temperature and pressure application range was not wide enough. Nicolas *et al.*[3] calculated the mutual solubilities for the CO₂-H₂O system in a wide temperature and pressure range (285.15—373.15K, 0.1—60MPa) by using a solubility formulation based on "true" equilibrium constants (K) and RK EOS. Values of K vary with temperature and pressure. The temperature and pressure dependence of K was taken into account as the formulation in the paper[3]. The comparison with the experimental data shows that the calculation is reliable at the temperature lower than 323.15K. However, the calculation of the water content has not been verified at higher temperatures (> 348.15K) and pressures (> 5MPa) because of the limited experimental data. Chapoy *et al.*[7] combined the Valderrama modification of the PT EOS with non-density-dependent mixing rules (NDD) to calculate fugacities in all fluid phases, and the hydrate phase was modeled by the solid solution theory of van der Waals and Platteeuw. The fugacity of water in the empty hydrate lattice was calculated using Kihara potential function to describe the encaged guest-water interaction. The fugacity of ice was calculated from the saturation fugacity of water at the system temperature with the Poynting correction. Results were in good agreement with the experimental data, but the temperature and pressure ranges (273.15—353.15K, below 12MPa) were a bit narrow.

In addition, the γ - ϕ approach can be used to calculate the mutual solubilities for the CO₂-H₂O system reliably, but the density of the H₂O-rich phase cannot be obtained from G^E models directly.

For the ϕ - ϕ approach, Shyu *et al.*[53] correlated

phase equilibria for the CO₂-H₂O system based on PR EOS with the Wong-Sandler mixture combining rule (W-S MCR). In the W-S MCR, van Laar model is used to calculate the excess Gibbs energy with three parameters, two energy parameters (a simple two-parameter G^E model is sufficient to obtain the equilibrium composition of the liquid phase) for the liquid phase and one interaction parameter (appearing in the cross second virial coefficient) for the gas phase. The phase behavior for the CO₂-H₂O system over a wide range of temperature (298.15–623.15K) and pressure (1–100MPa) was studied, and the calculated solubility of CO₂ in water was accurate. Valtz *et al.* [35] combined PR EOS with W-S MCR to calculate the VLE for the CO₂-H₂O system at the temperature and pressure of 278.2–318.2K, 0.464–7.963MPa. NRTL local composition model was used to obtain the excess molar Gibbs free energy. The calculated vapour composition was accurate, especially at low temperatures.

Molecular-based statistical associating fluid theory equation of state (SAFT-EOS) was also used to study the phase equilibria for the CO₂-H₂O system. The essence of SAFT EOS is that the residual Helmholtz energy is described by a sum of expressions to account for not only the effects of short-range repulsions and long-range dispersion forces but also the effects of chemically bonded aggregation (*e.g.* formation of chemically stable chains) and association and/or salvation (*e.g.* hydrogen bonding) between different molecules (or chains). The residual molar Helmholtz energy has contributions from the formation of hard spheres and chains, dispersion (attraction), and association[54]. Valtz *et al.* [35] calculated the VLE for the CO₂-H₂O system over the temperature and pressure of 278.2–318.2K, 0.464–7.963MPa by using SAFT-VR EOS which is based on a variable range square-well potential. The calculated CO₂ solubility agrees with the experimental data well. However, the predicted water content in the CO₂-rich vapour phase deviated from experimental data, especially at low temperatures and high pressures, which may be due to the assumption of non-association sites between water and CO₂, and non-effect of the temperature on square-well potential parameters. Ji *et al.* [51] represented the density and the composition of the equilibrium phases in the CO₂-H₂O system from 285 to 473K and up to 60MPa by using SAFT1 EOS. The calculated results agree with the experimental data in the temperature range of 288.15 to 373.15K. However, the calculated results at high temperatures (>373.15K) and high pressures show some disagreement with the experimental data for both CO₂-rich and H₂O-rich phases. This may be because that the association term was used to account for association and dipolar interactions between H₂O molecules and quadrupolar interactions between CO₂ molecules. As the temperature increases, the association term cannot describe the dipolar interactions between H₂O molecules and quadrupolar interactions between CO₂ molecules.

3.1.2 CO₂-H₂O-NaCl system

Carbon dioxide solubilities in aqueous NaCl solutions have been studied. Thermodynamic models

proposed recently are introduced in the following text.

(1) Models based on the modified PT EOS. Zuo and Guo[55] extended PT EOS to electrolyte solutions at high pressures and correlated the gas solubility in electrolyte solutions. Carbon dioxide solubilities in aqueous NaCl solutions at 394.15K and at pressures up to 140MPa were calculated and the salt effect on the gas solubility was predicted reliably[55]. Gu[29] used the modified PT EOS to calculate CO₂ solubilities in aqueous NaCl solutions in the temperature range of 303.15–323.15K, pressure range of 0.1–6.0MPa, and the salt concentration range of 0.5–2.0mol·L⁻¹. The calculated and experimental solubilities show a good agreement.

(2) Kiepe *et al.* [33] calculated VLE for the CO₂-H₂O-NaCl system at the temperature and pressure of 313.15–353.15K, 0–10MPa by using the combination of PSRK group contribution EOS with LIFAC model to account for the effect of strong electrolytes on the activity coefficients of nonelectrolytes. The prediction is in good agreement with the experimental data. Kiepe *et al.* [56] calculated the gas solubility in the CO₂-H₂O-NaCl system from 313.15 to 523.15K and from 0.01 to 60MPa by coupling PSRK group contribution EOS with group contribution model LIFAC. The calculated and experimental gas solubilities agree well at temperatures lower than 353.15K, but at higher temperatures (>353.15K) and pressures (>40MPa), the calculated gas solubility shows some discrepancies from the experimental data.

(3) Duan and Sun[42] calculated the solubility of CO₂ in aqueous NaCl solutions at temperatures from 273 to 533K, pressures from 0 to 200MPa, and ionic strength from 0 to 4.3mol·L⁻¹ by an improved model. The model was based on a specific particle interaction theory for the liquid phase and an accurate equation of state for the vapour phase. Properties of CO₂-H₂O-CaCl₂ and CO₂-seawater systems were predicted without any additional parameters, but the prediction at high temperatures and pressures has not been verified yet because of the scarcity of the experimental data.

(4) Ji *et al.* [51] used the extension of SAFT1 (SAFT1-RPM) to represent the gas solubility and densities of the CO₂-H₂O-NaCl system from 298 to 373K and up to 20MPa. The calculated results agree with the experimental data at the pressure lower than 10MPa, but the calculated CO₂ solubility disagrees with the experimental data at high temperatures and pressures. In addition, the calculated density at 353.15K in H₂O-rich phase by SAFT1-RPM disagrees with the experimental data.

Among the four models described above, the former three belong to the γ - ϕ approach and the last one belongs to the ϕ - ϕ approach. The SAFT1-RPM theory used by Ji *et al.* [51] is a promising approach because densities of the electrolyte solutions can be obtained simultaneously.

The review of the thermodynamic models for the CO₂-H₂O and CO₂-H₂O-NaCl systems shows that the molecular-based statistical associating fluid theory equation of state (SAFT-EOS) is a promising model. SAFT1-RPM theory used by Ji *et al.* [51] is one sample,

but it still cannot describe the phase behavior and density at high temperatures and pressures for the $\text{CO}_2\text{-H}_2\text{O-NaCl}$ system accurately. Moreover, natural waters often contain ions more than Na^+ and Cl^- , for example, K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , CO_3^{2-} [42], which requires to study the phase equilibrium and densities of aqueous solutions with CO_2 and multi-ions under the geological conditions. Some improvements may be made by using the SAFT EOS coupling other EOS or activity coefficient models. It is because that hydration and association cannot be neglected for electrolyte solutions at high temperatures and pressures, and the thermodynamic model can be modified based on the synergistic action of association and hydration to get reliable phase equilibrium.

3.2 Calculations with selected thermodynamic models

As Pitzer's equation and the electrolyte NRTL activity coefficient model have been proven successful in calculating the activity coefficient of the electrolyte aqueous solution, and they haven't been used to study the phase equilibria of $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-H}_2\text{O-NaCl}$ systems. Three different models are used to calculate the vapor-liquid phase equilibrium of $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-H}_2\text{O-NaCl}$ systems in this paper, and the calculation results are compared with the experimental data to evaluate the experimental data further more.

In the first thermodynamic model, the electrolyte NRTL (ELECNRTL) activity coefficient model [57—60] is used to calculate the activity coefficient of the aqueous solution, the Redlich-Kwong equation of state [61] is used to calculate the fugacity coefficient for the vapor phase. The pair parameters of the ELECNRTL model are obtained by regressing vapor pressure and mole fraction data at 100°C . The second model (ENRTL-HG) is similar to the ELECNRTL method, except it uses the Helgeson model for standard properties calculations. The Helgeson model should provide more accurate enthalpy and Gibbs free energy up to high temperature and pressure. Here SUPCRT92 [62] is used to calculate the standard properties. In the third model (PITZ-HG), the Pitzer activity coefficient model [63—65] is used to calculate the activity coefficient of the aqueous solution, the parameters for the Pitzer model are available from Pitzer's series [63—65] on the thermodynamics of electrolytes. SUPCRT92 [62] is used for standard properties calculations, and the Redlich-Kwong-Soave equation of state [66—68] is used to calculate the vapor phase fugacity coefficient. In all the three methods, the solubility of CO_2 is modeled using Henry's law.

3.2.1 $\text{CO}_2\text{-H}_2\text{O}$ system

The phase equilibrium of $\text{CO}_2\text{-H}_2\text{O}$ system in wide temperature and pressure ranges is firstly calculated by the three different models. For the interests of CO_2 geological sequestration, only the results under three temperatures (323.15, 373.15, 473.15K) are represented. The pressure conditions studied for this system is from 0 to 80MPa, and the results are shown in Fig.2.

As is shown in Fig.2, for the calculated CO_2

solubility in H_2O -rich phase under 323.15, 373.15 and 473.15K, the calculated CO_2 solubility under the pressures below 10MPa agrees with the experimental data quite well. However, when the pressure is above 10MPa, there are great discrepancies. And the discrepancies are more obvious as the temperature increases. Although the calculated results don't agree with the experimental data very well at high pressures, the temperature and pressure dependence of the CO_2 solubilities is consistent with the experimental data. From the comparison of our calculated results with the experimental data, it can be seen the three models can't describe the CO_2 solubility of high pressures very well. So the modifications should be made, new parameters should be obtained. Meanwhile, as is described in the foregoing review, the experimental data of high temperatures and pressures are very scarce, which will bring more difficulties for the parameter fitting in the thermodynamic models to the experimental data.

For the calculated water content in CO_2 -rich phase at 323.15K, the results below 10MPa agrees with the experimental data very well, but there are great discrepancies above 10MPa. The results at 373.15K show that calculated water content data below 20MPa are consistent with the experimental data. And the agreements of the results at 373.15K are much better than that at 323.15K. Considering the calculation results at 473.15K, it can be also found that water content data can't be obtained by the calculation using the three models when the pressure is below 3.1MPa. It is assumed that the liquid phase has been transformed to vapor phase. While as the pressure increases, the calculated water content data agree with the experimental data quite well, much better than that at the other two temperatures. As the experimental data at high temperatures and pressures are very scarce, here it is a bit difficult to validate the pressure dependence of the calculated water content data at very high pressures.

3.2.2 $\text{CO}_2\text{-H}_2\text{O-NaCl}$ system

The phase equilibria of $\text{CO}_2\text{-H}_2\text{O-NaCl}$ system under the temperature of 313.15 and 333.15K is also calculated. The concentrations of the NaCl are $0.52\text{mol}\cdot\text{L}^{-1}$ and $3.997\text{mol}\cdot\text{L}^{-1}$. Also the pressures are up to 80MPa. The comparison of the calculated results with the experimental data is shown in Fig.3.

From Fig.3 it is found that for the NaCl concentration of $0.52\text{mol}\cdot\text{L}^{-1}$, the calculated results by the three different models agree well with the experiment data. And the PITZ-HG model brings the best agreement. For the NaCl concentration of $3.997\text{mol}\cdot\text{L}^{-1}$, the calculated results by ELECNRTL and ENRTL-HG models show good agreements with the experimental data. But there are great discrepancies between the calculation results and the experimental data when using PITZ-HG model, which also shows that the PITZ-HG model should be modified when using in high salt concentrations. In general, the three models not only well describe the pressure effect and temperature effect on the CO_2 solubility, but also the salting-out effect. At constant pressure, the solubility of

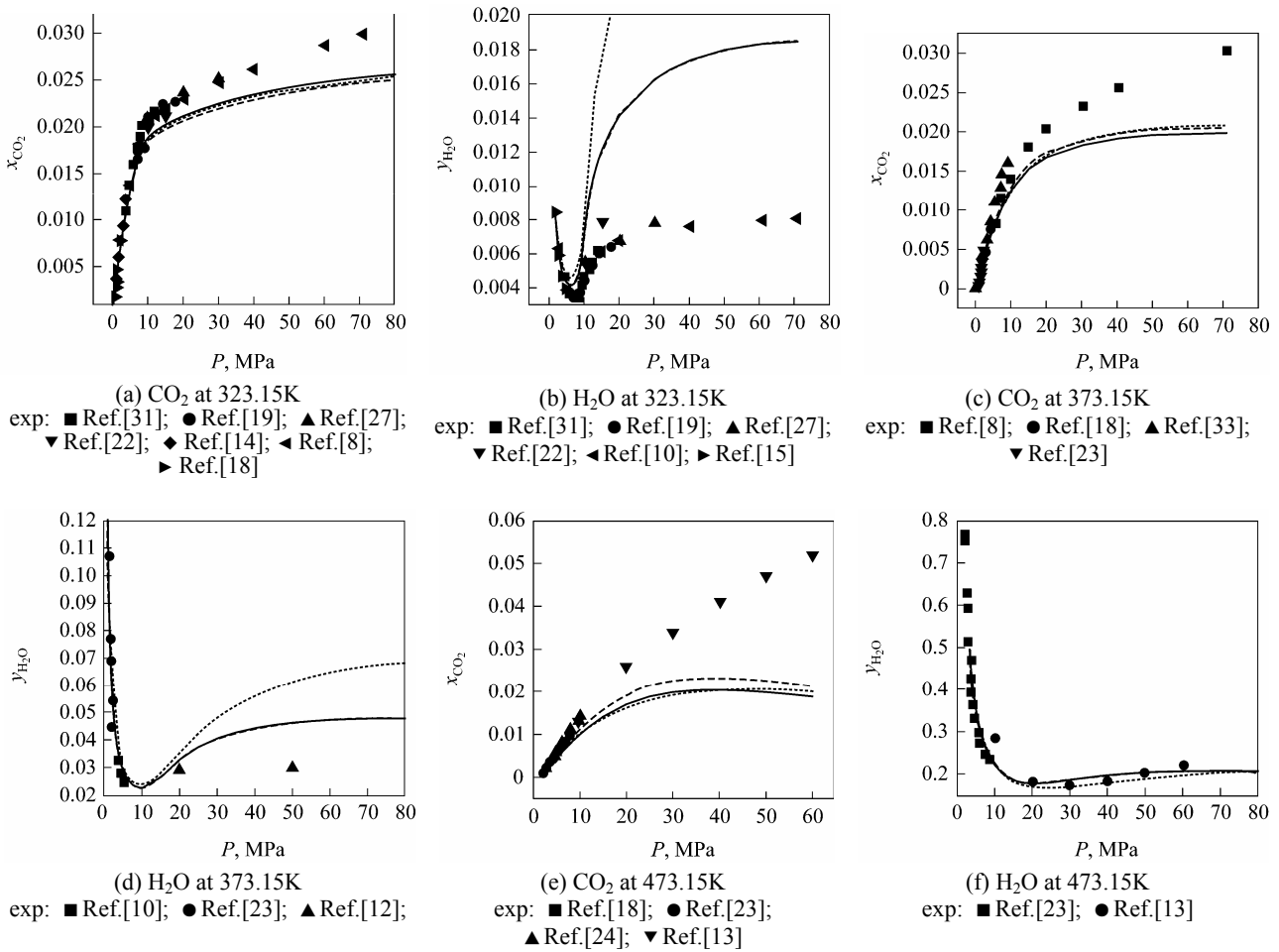


Figure 2 Mole fractions of CO₂ in H₂O-rich phase and mole fractions of H₂O in CO₂-rich phase for CO₂-H₂O system at different temperatures

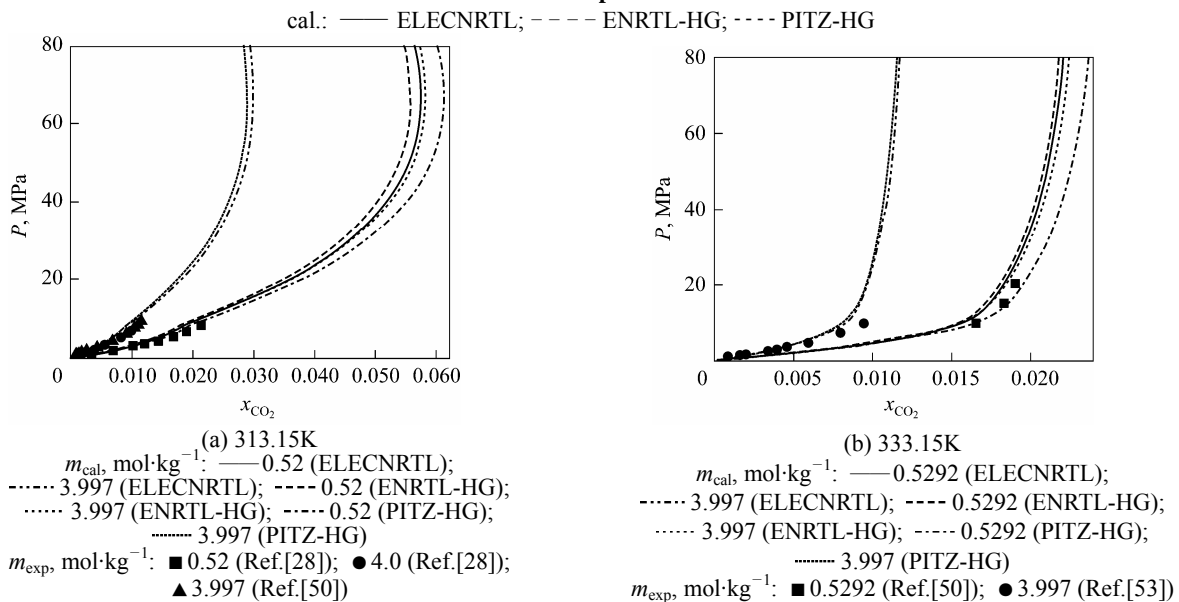


Figure 3 Mole fractions of CO₂ in H₂O-rich phase for CO₂-H₂O-NaCl system at 313.15 and 333.15K

CO₂ in the aqueous solution decreases with increasing salt concentrations.

From the reviews of the existing models and the calculations with selected three thermodynamic models,

it can be found that the existing thermodynamic models can nearly satisfy the needs of the calculations for the sequestration capacity in the temperature and pressure range for disposal of CO₂ in deep saline aquifers.

But for the temperature and pressure as high as 398.15K and 31.5MPa, which may reach in the abandoned oil and gas reservoirs, the models can't obtain very accurate results. In order to meet the requirements of the geological sequestration applications, more accurate calculations at high temperatures and pressures are needed.

4 MOLECULAR SIMULATION

With the development of simulation methodology and the increasing performance of computers, molecular simulation is becoming a more and more attractive tool for fluid property predictions. Because of the well-established basis of statistical mechanics, molecular simulation may provide, in the future, better prediction capabilities than any classical thermodynamic models as well as a better understanding of the relationship between molecular level properties and the thermodynamic behavior of substances. Due to the evolution of molecular simulation methods, simulations applying relatively complex intermolecular interaction models have become possible. However, to get reliable statistical averages for the thermodynamic properties within reasonable computing time, simplified intermolecular interaction models, so-called "effective pair potentials", are predominantly used in simulations[69]. Monte Carlo simulation (MC) is a modern research approach in chemical thermodynamics. Gibbs ensemble Monte Carlo (GEMC) simulations have been used to calculate the phase equilibrium properties for fluids and fluid mixture, such as vapour heat, composition and density of vapour phase and liquid phase, and so on.

4.1 CO₂-H₂O system

Vorholz *et al.*[70] applied NVT- and NpT-GEMC simulations to describe the vapour-liquid equilibrium of water (323.15—573.15K, 0.002—12.5MPa), carbon dioxide (230.15—290.15K, 1.02—5.67MPa) and their binary mixtures (348.15—393.15K, 2.500—20.265MPa). The GEMC simulation for the pure substances of water and carbon dioxide shows that for water, the SPC- and TIP4P models obtain superior results for the vapour pressure compared to the SPC/E model. For carbon dioxide, the EPM2 potential model was used, and VLE of the CO₂-H₂O system was predicted by using the SPC- as well as the TIP4P model for water and the EPM2 model for carbon dioxide. In the temperature and pressure range considered, the predicted compositions of the coexisting phases at equilibrium are in agreement with the experimental data and the calculated results of thermodynamic models. From the simulated P-ρ diagram at the temperature of 393.15K, it can be seen that the simulated densities of the vapour phase (SPC-H₂O-EPM2-CO₂ and TIP4P-H₂O-EPM2-CO₂) are in good agreement with the experimental data, but the simulated densities of the liquid phase show some disagreement with the experimental data and the calculated results of thermodynamic models. In a word, Vorholz *et al.* succeeded in using GEMC simulation to describe the

phase equilibria of the CO₂-H₂O system at high temperatures and pressures, which also proved the advantages of the molecular simulation. In addition, it also provides some references for the prediction of the solubility of other gases by GEMC simulation.

4.2 CO₂-H₂O-NaCl system

Vorholz *et al.*[71] studied the solubility of carbon dioxide in aqueous solutions of sodium chloride by NVT- and NpT-GEMC simulations at 373, 393 and 433K, respectively, and at pressures up to 10MPa. They also calculated the densities of the CO₂-H₂O-NaCl coexisting phase at the temperature of 393.15K. The intermolecular forces were approximated by effective pair potentials (SPC and TIP4P models for water, EPM2 potential model for carbon dioxide, and several pair potentials for sodium chloride). The pressure range considered in this study is not wide enough, and the agreement between the simulation results and the experimental data is not good, but an improvement can be achieved by introducing binary interaction parameters into unlike pair potentials. The potential models chosen in this work provide references for other studies on the carbon dioxide solubilities in aqueous NaCl solutions at the temperature and pressure of interest.

GEMC simulations can complement experimental data at high temperatures and pressures, and the choice and improvement of the effective pair potentials are two key factors to reach a success simulation.

5 CONCLUSIONS

The phase equilibria and densities of the CO₂-H₂O and CO₂-H₂O-NaCl systems in a wide temperature and pressure range (273.15—473.15K, 0—60MPa) are reviewed from experimental data and thermodynamic models. The following conclusions are drawn:

(1) Experimental data at high temperatures and pressures are scarce for the studied two systems, therefore, it is significant to measure new experimental data at high temperatures and pressures in order to fit the parameters of a new semi-empirical model or to verify the prediction of the existing models.

(2) Among the existing thermodynamic models, no models can represent the phase equilibria at high temperature and pressure quite well. Besides the research on CO₂-H₂O and CO₂-H₂O-NaCl systems, it is also necessary to study the phase equilibrium and the densities of the aqueous solutions with CO₂ and multi-ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, CO₃²⁻, and so on) under the geological conditions of a wide temperature and pressure range.

(3) Three different models (ELECRTL, ENRTL-HG, PIZ-HG) are used to represent the phase behavior of CO₂-H₂O and CO₂-H₂O-NaCl systems. For CO₂-H₂O system, our calculated mutual solubilities of CO₂ and H₂O showed that the agreements between the calculation results and the experimental data are very good at low and medium pressures (0—20MPa). When the pressure is above 20MPa, there are

great discrepancies. But for the calculated water content data at 473.15K, the calculated results agree with the experimental data quite well. The three models should be modified and more accurate parameters should be obtained when using in high pressures. For CO₂-H₂O-NaCl system, PITZ-HG model shows better results than ELECNRTL and ENRTL-HG models at the NaCl concentration of 0.52mol·L⁻¹. But for the NaCl concentration of 3.997mol·L⁻¹, using ELECNRTL and ENRTL-HG models give better results than using PITZ-HG model.

(4) From the reviews of the available experimental data and the thermodynamic calculations, it can be seen that the data and the models can satisfy the needs of the calculations for the sequestration capacity in the temperature and pressure range for disposal of CO₂ in deep saline aquifers. But considering the injection of carbon dioxide into depleted hydrocarbon reservoirs, more experimental data and more accurate thermodynamic calculations are needed at high temperatures and pressures (more than 398.15K and 31.5MPa).

(5) Molecular simulation (GEMC) plays an important role on the study of VLE and complementing experimental data. But studies for CO₂-H₂O and CO₂-H₂O-NaCl systems show an unsatisfying result. The choice and the improvement of the effective pair potentials are two key factors to improve simulations.

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