Modeling mass transfer of CO₂ in brine at high pressures by chemical potential gradient

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To investigate long-term CO₂ behavior in geological formations and quantification of possible CO₂ leaks, it is crucial to investigate the potential mobility of CO₂ dissolved in brines over a wide range of spatial and temporal scales and density distributions in geological media. In this work, the mass transfer of aqueous CO₂ in brines has been investigated by means of a chemical potential gradient model based on non-equilibrium thermodynamics in which the statistical associating fluid theory equation of state was used to calculate the fugacity coefficient of CO₂ in brine. The investigation shows that the interfacial concentration of aqueous CO₂ and the corresponding density both increase with increasing pressure and decreasing temperature; the effective diffusion coefficients decrease initially and then increase with increasing pressure; and the density of the CO₂-dissolved brines increases with decreasing CO₂ pressure in the CO₂ dissolution process. The aqueous CO₂ concentration profiles obtained by the chemical potential gradient model are considerably different from those obtained by the concentration gradient model, which shows the importance of considering non-ideality, especially when the pressure is high.

CO₂ geological sequestration, dissolution, non-equilibrium thermodynamics, mass transport, diffusion, density, SAFT EoS

1 Introduction

CO₂ geological storage is a promising means to mitigate CO₂ emission [1–5] and storage in deep saline aquifers appears to hold the largest potential capacity [4, 6–8]. The sequestration capacity, long-term CO₂ behavior in receptor formations, and the quantification of possible CO₂ leaks are the main concerns [2, 4, 9, 10], and there remains a need to study the potential mobility of CO₂ dissolved in brines over a wide range of spatial and temporal scales [4, 9, 11], the CO₂ concentration distribution in saline aquifers, as well as the density distribution in geological media [8]. This highlights the significance of research on CO₂ dissolution and

the mass transfer of CO₂ dissolved in brines.

Numerous investigations of the mass transfer of CO₂ in high-pressure water or brines have been pursued in order to further simulate the geological and ocean CO₂ disposal processes [8, 12–19]. It has been shown that the dissolution of CO₂ in brines increases the density, and then induces density-driven natural convection [8, 12, 16–18], and the density-driven natural convection then significantly accelerates the diffusion of CO₂ in the brine [8, 16–18]. Yang and Gu [8] investigated experimentally the dissolution of CO₂ in brine at elevated pressures and described the mass transfer of CO₂ in brine using a modified diffusion equation with an effective diffusion coefficient. The effective diffusion coefficients obtained were two orders of magnitude larger than the molecular diffusivity of CO₂ in water [8], which indicates that the density-driven natural convection

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greatly accelerates the mass transfer of CO₂ in brines.

In a theoretical study, Fick's second law was used to describe the mass transfer of CO₂ in brines under geological conditions, and the concentration gradient was used empirically as the driving force [8]. However, it is well known that the driving force should be the chemical potential gradient, and for an ideal diluted homogeneous solution with one component, the chemical potential gradient can be simplified to be the concentration gradient [20]. In practice, the investigated system is generally a mixture, and sometimes, the pressures may be up to several hundred bar. In this case, chemical potential gradient should be used as the driving force. Our previous work based on non-equilibrium thermodynamics [21–23] also reveals that it is necessary to consider the non-ideality of such complex systems.

In this paper, the mass transfer of CO₂ in brines is investigated by means of a chemical potential gradient model based on non-equilibrium thermodynamics in which SAFT1-RPM EoS [24] is used to calculate the fugacity coefficient of aqueous CO₂ in brines and the solution densities. The results obtained in this work are compared with those from the concentration gradient model to illustrate the importance of combining the thermodynamic model with a mass transfer model.

2 Thermodynamic model

In our previous review article [25], it was shown that the molecular-based statistical associating fluid theory (SAFT) equation of state (EoS) is a promising model for complicated systems at high pressures. The phase equilibria and densities in the CO₂-H₂O and CO₂-H₂O-NaCl systems have been investigated using SAFT1-RPM EoS in our previous work [24]. Since the main component of brine is NaCl [8], in this work, the thermodynamic properties and phase equilibria of the CO₂-brine system were assumed to be those of the CO₂-H₂O-NaCl system, and SAFT1-RPM EoS was used to calculate the corresponding phase equilibrium, the fugacity coefficient of aqueous CO₂ in brine, and the densities of CO₂-brine systems.

In SAFT1-RPM EoS [24], the dimensionless residual Helmholtz energy is defined as

$$\tilde{a}^{\text{res}} = \tilde{a}^{\text{seg}} + \tilde{a}^{\text{assoc}} + \tilde{a}^{\text{chain}} + \tilde{a}^{\text{ion}} \quad (1)$$

where the superscripts refer to terms of the residual, segment, association, chain, and ionic interactions, respectively. For non-electrolytes, the ionic contribution is set equal to zero. The segment, chain, and ion terms have been described in detail elsewhere [26–29].

Any other thermodynamic properties can be calculated from this residual Helmholtz energy. For example, the fugacity coefficient of component *i* can be derived as:

$$\ln \phi_i = \tilde{a}^{\text{res}} + \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} - \sum_j x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j} \right)_{T, \rho, x_{k \neq j}} + Z - 1 - \ln Z \quad (2)$$

where *Z* is the compressibility factor and calculated using

$$Z = 1 + \rho \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho} \right)_{T, x} \quad (3)$$

For the CO₂-H₂O-NaCl system, the detailed modeling of each component and mixtures as well as the corresponding parameters have been described in our previous work [24].

3 Mass transfer model with chemical potential gradient

3.1 Model description

In an ideal dilute homogeneous solution of one component, the flux *J* (mol m⁻² s⁻¹) and the concentration changes for a non-charged substance in the *x*-direction are described by the first and second Fick's laws as shown in Eqs. (4) and (5) [20]:

$$J = -D \frac{\partial c}{\partial x} \quad (4)$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (5)$$

where *D* (m² s⁻¹) is the diffusion coefficient, *c* (mol m⁻³) is the concentration, *t* (s) is the time, and *x* (m) is the distance.

In chemical systems other than ideal solutions or mixtures, the driving force of diffusion for each species is the chemical potential gradient. According to non-equilibrium thermodynamics, the flux *J* of a substance in the direction *x* expressed as changes of activity of the substance (*a_i*) by volume per area per time is proportional to the product of activity and chemical potential gradient [20], i.e.

$$J = -\frac{Da_i}{RT} \frac{\partial \mu_i}{\partial x} \quad (6)$$

For a time-dependent transport process, assuming the diffusion coefficient *D* to be a constant at a certain temperature and pressure, combining Eq. (6), Eq. (7) which describes $\partial a_i / \partial t$ can be derived [20].

$$\frac{\partial a_i}{\partial t} = -\frac{\partial J}{\partial x} = \frac{D}{RT} \frac{\partial}{\partial x} \left(a_i \frac{\partial \mu_i}{\partial x} \right) = \frac{D}{RT} \left[\frac{\partial a_i}{\partial x} \frac{\partial \mu_i}{\partial x} + a_i \frac{\partial^2 \mu_i}{\partial x^2} \right] \quad (7)$$

where *a_i* and *μ_i* are the activity and chemical potential of component *i*, respectively.

According to the definition of activity and chemical potential [30], we have

$$a_i = \frac{f_i}{f_i^0} \quad (8)$$

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{f_i^0} = \mu_i^0 + RT \ln a_i \quad (9)$$

where f_i and f_i^0 are the fugacity and standard fugacity of component i , respectively. μ_i^0 is the standard chemical potential of the component i .

The fugacity of component i is described as

$$f_i = \phi_i x_i P \quad (10)$$

At a certain temperature and pressure, both μ_i^0 and f_i^0 are constants. Combining Eq. (7) with Eqs. (8) and (9), Eq. (11) can be derived.

$$\frac{\partial f_i(x,t)}{\partial t} = D \frac{\partial^2 f_i(x,t)}{\partial x^2} \quad (11)$$

where D is the diffusion coefficient of component i .

If we let $\tilde{f}_i = \phi_i x_i$, at a constant pressure, we have

$$\frac{\partial \tilde{f}_i(x,t)}{\partial t} = D \frac{\partial^2 \tilde{f}_i(x,t)}{\partial x^2} \quad (12)$$

3.2 Diffusion coefficient

For the investigated process, the dissolution of CO_2 in brines increases the density and then induces the density-driven natural convection which accelerates the diffusion of CO_2 in brines [8, 12, 16–18]. It is necessary to consider both the convective molar flux and the molecular diffusion molar flux in order to model the mass-transfer process accurately. In order to investigate the magnitude of the effect of the density-driven natural convection on the CO_2 diffusion, and how important it is to adjust the non-ideality, in this paper, we used the method of Yang and Gu [8] with an effective diffusion coefficient D_{eff} to account for the joint effect of both the molecular diffusion and the density-driven natural convection on the mass transfer of CO_2 in brines, which is valid for the early stages of the CO_2 dissolution process. The effective diffusion coefficient was obtained from an iterative calculation based on the experimental kinetic data of the CO_2 dissolution in brines taken from Yang and Gu [8].

In the work of Yang and Gu [8], the CO_2 dissolution process was performed in a PvT cell with a cross-sectional area A , and the CO_2 pressures P_t at different time t were measured. The number of moles of dissolved CO_2 (n_t) can be determined from the gaseous pressure at time t and the initial experimental conditions. Based on mass balance, we have:

$$\int_0^x c_{\text{CO}_2(\text{aq})} A dx = n_t \quad (13)$$

where $c_{\text{CO}_2(\text{aq})}$ (mol m^{-3}) is the molar concentration of aqueous CO_2 in brines, A (m^2) is the contact area of gaseous CO_2 with brine which was assumed to be the cross-sectional area of the cell, and x (m) is the mass transfer distance.

In the work of Yang and Gu [8], only the experimental kinetics data after 180 s were used to analyze the mass-transfer process of CO_2 in the brine. In this paper, we also took the kinetic data after 180 s.

3.2.1 Initial and boundary conditions

The initial condition is given by Eq. (14)

$$\tilde{f}_i(x,t)|_{t=0} = \begin{cases} \tilde{f}_{i0} & (x=0) \\ 0 & (0 < x \leq H) \end{cases} \quad (14)$$

In Eq. (14), $\tilde{f}_{i0}$ is the product of the molar fraction and fugacity coefficient for the saturated aqueous CO_2 at a certain temperature and pressure. H is the brine phase height in the work of Yang and Gu [8] which is equal to 0.0442 m.

It was assumed that the interface was instantaneously saturated with CO_2 , and the fugacity coefficients were calculated with SAFT1-RPM EoS [24] from temperature, pressure and the corresponding saturation concentration. For the bottom of the experimental PvT cell, the boundary condition is

$$\frac{\partial \tilde{f}_i(x,t)}{\partial x} \Big|_{x=H} = 0 \quad (t > 0) \quad (15)$$

3.2.2 Numerical solution

The semi-infinite medium model was applied, and the analytical solution for Eq. (12) was obtained by Crank [31] as

$$\tilde{f}_i(x,t) = \tilde{f}_{i(\text{int})} - \frac{2\tilde{f}_{i(\text{int})}}{\sqrt{\pi}} \int_0^{x/(2\sqrt{D_{\text{eff}}t})} e^{-s^2} ds \quad (16)$$

In Eq. (16), $\tilde{f}_{i(\text{int})}$ is the $\phi_i x_i$ of component i at the interface. At a certain temperature and pressure, combining the thermodynamic model, the concentration profiles of the aqueous CO_2 and the effective diffusion coefficients can be obtained from the integral equation Eq. (13) by iteration. The detailed steps of the iterative procedures are shown in Figure 1.

In the calculation of the effective diffusion coefficient D_{eff} and real diffusion distance x_{real} , the direct iterative search method was used. In this method, we assumed that the range of D_{eff} was from 1.0×10^{-9} to $1.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, and both the initial value and step length of D_{eff} were set to be $1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

The range of x_{real} was taken from 0 to x_{limit} (x_{limit} was defined in the following text), and the initial value and step length of diffusion distance x_{real} were set to be 0 and $1.0 \times 10^{-3} \text{ m}$, respectively. As shown in Figure 1, to calculate both

Figure 1 The detailed steps of the iterative procedures for the determination of the effective diffusion coefficient.

D_{eff} and x_{real} , four steps needed in each loop. The details are shown in the following text.

(1) The function relationship of the $\tilde{f}_i(x, t)$ at a certain temperature and pressure with the concentration of aqueous CO_2 in brine was fitted to the results calculated with SAFT1-RPM EoS [24] as shown in Eq. (17).

$$\tilde{f}_i(x, t) = g [x_{\text{CO}_2(\text{aq})}] \quad (17)$$

where $x_{\text{CO}_2(\text{aq})}$ is the molar fraction of aqueous CO_2 in the brine.

(2) Set the upper limit of integral in Eq. (16) as z_{end} , i.e.

$$z_{\text{end}} = \frac{x}{2\sqrt{D_{\text{eff}}t}}. \text{ We took the initial value and step length of}$$

z_{end} as 0 and 1.0×10^{-3} m, respectively. z_{end} was determined from iteration by solving Eq. (16) coupled with Eq. (17). At a certain time, when the mole fraction of aqueous CO_2 meets the requirement ($< 1.0 \times 10^{-6}$), z_{end} was obtained.

(3) The limiting value of the diffusion distance x_{limit} was determined from $x_{\text{limit}} = 2z_{\text{end}}\sqrt{D_{\text{eff}}t}$ according to the maximum value of the upper limit of integral z_{end} in Eq. (16) obtained in Step (2). The real maximum value of the diffusion distance should be no more than the limiting value of the diffusion distance x_{limit} , i.e. $x_{\text{real}} \leq x_{\text{limit}}$.

(4) The integral equation $\int_0^{x_{\text{real}}} c_{\text{CO}_2(\text{aq})} A dx$, in which $c_{\text{CO}_2(\text{aq})}$ is the molar concentration of aqueous CO_2 in brine,

was solved numerically using the built-in “quad” in the MATLAB program by combining Eqs. (16) and (17). Then the integral value of $\int_0^{x_{\text{real}}} c_{\text{CO}_2(\text{aq})} A dx$ was compared with the number of moles of dissolved CO_2 (n_t) from the experiment. If the inequality $\left| \int_0^{x_{\text{real}}} c_{\text{CO}_2(\text{aq})} A dx - n_t \right| < 1.0 \times 10^{-8}$ was met, the D_{eff} and x_{real} in this iteration were the required effective diffusion coefficient and real diffusion distance, respectively. If the inequality $\left| \int_0^{x_{\text{real}}} c_{\text{CO}_2(\text{aq})} A dx - n_t \right| < 1.0 \times 10^{-8}$ was not met, the iterative search was continued until the inequality $\left| \int_0^{x_{\text{real}}} c_{\text{CO}_2(\text{aq})} A dx - n_t \right| < 1.0 \times 10^{-8}$ was met.

The densities of the CO_2 -dissolved brines were then calculated from the concentration profiles and the corresponding temperature and pressure.

4 Results and discussion

4.1 Equilibrium properties of the CO_2 -brine system

The equilibrium concentrations of CO_2 in NaCl solutions and the densities of CO_2 -saturated NaCl solutions at two temperatures and different pressures were calculated with SAFT1-RPM EoS and are shown in Figures 2 and 3. The experimental results [8] of equilibrium concentration of CO_2 in brine and the density of CO_2 -saturated brine are also shown in Figures 2 and 3 as symbols. The calculated results

Figure 2 Equilibrium concentration of CO₂ in brine versus equilibrium pressure. Experimental data: ■ 300.15 K [8]; ▲ 331.15 K [8]; — calculated, 300.15 K; - - - calculated, 331.15 K.

Figure 3 Density of CO₂-saturated brine versus equilibrium pressure. Experimental data: ■ 300.15 K [8]; ▲ 331.15 K [8]; — calculated, 300.15 K; - - - calculated, 331.15 K.

were compared with experimental data, and the average

relative deviation (ARD (%)) = $\frac{100}{N} \sum_{i=1}^N \frac{|x_{p,\text{exp}} - x_{p,\text{cal}}|}{x_{p,\text{exp}}}$, where

N is the number of data points, x_p is the property of density or CO₂ equilibrium concentration, and the subscripts “exp” and “cal” represent experimental and calculated results, respectively) in CO₂ equilibrium concentration is 6.72% and ARD in density is 0.22%. The comparison shown in Figures 2 and 3 and the corresponding ARDs imply that the thermodynamic properties and the phase equilibrium of the CO₂-brine system can be assumed to be those of the CO₂-H₂O-NaCl system. Meanwhile, both the CO₂

equilibrium concentrations in brine and the densities of CO₂-saturated brine increase with increasing pressure and decreasing temperature.

4.2 Interfacial thermodynamic properties

We assumed that the interface was instantaneously saturated with CO₂. Based on the experimental conditions listed in Table 1 from Yang and Gu [8], the interfacial thermodynamic properties of aqueous CO₂ concentrations, $\tilde{f}_i$ of aqueous CO₂, and the CO₂-saturated brine densities were calculated with SAFT1-RPM EoS and shown in Figures 4–6.

Figure 4 The interfacial concentrations of the aqueous CO₂ in brines calculated in this work and those from Yang and Gu [8]. ○ Yang and Gu [8]; ■ calculated in this work.

Table 1 Experimental conditions and results in the study of Yang and Gu [8]

Test	T (K)	Initial CO_2 pressure (MPa)	Initial CO_2 volume (m^3)	D_{eff} ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)
1	300.15	3.668	1.0116×10^{-4}	170.7
2	300.15	2.558	9.7480×10^{-5}	175.7
3	300.15	1.786	9.7050×10^{-5}	183.2
4	331.15	5.647	1.0044×10^{-4}	258.7
5	331.15	4.516	1.0231×10^{-4}	250.2
6	331.15	3.537	1.0331×10^{-4}	269.8

Figure 5 $\phi_i X_i$ of the aqueous CO_2 in brines at the interface calculated with SAFT1-RPM. **Figure 6** The interfacial densities of CO_2 -saturated brine calculated with SAFT1-RPM.

As shown in Figure 4, the interfacial concentration of aqueous CO_2 in brines increases with increasing pressure and decreasing temperature. For Tests 1, 4, 5 and 6, the

concentrations of the aqueous CO_2 at the interface at different pressures calculated in this work are lower than those from Yang and Gu [8] while for Tests 2 and 3, with in-

creasing pressure they are initially lower and then higher than those from Yang and Gu [8].

Figure 5 shows that the interfacial $\tilde{f}_i$ of aqueous CO₂ decreases with increasing pressure and temperature. While the interfacial densities of CO₂-saturated brines increase with increasing pressure and decreasing temperature, as shown in Figure 6, the effect of pressure on density is very small (< 0.1%).

4.3 Effective diffusion coefficient

The effective diffusion coefficients of aqueous CO₂ in brines obtained in this work are shown in Figure 7. The obtained results were based on the assumptions that were taken from Yang and Gu [8], i.e.

(1) After 180 s the pressure decay resulted entirely from the dissolution of CO₂ in the brine; (2) The interfacial concentration of aqueous CO₂ was the saturation value at the corresponding temperature and pressure; (3) The mass transfer area was the cross-sectional area A of the experimental cell.

The obtained effective diffusion coefficients were fitted to a polynomial as shown in Eq. (18). The fitting curves are also shown in Figure 7.

$$D_{\text{eff}} (10^{-9} \text{ m}^2 \text{ s}^{-1}) = C_1 + C_2 P + C_3 P^2 \quad (18)$$

where P is the pressure in MPa, C_1 , C_2 and C_3 are fitted parameters and are listed in Table 2.

As shown in Figure 7, with increasing pressure the effective diffusion coefficients decrease initially and then increase. Tewes and Boury [32] studied the CO₂ diffusion

coefficients in water at 313.15 K and at pressures between 3 to 8 MPa and obtained the same results, i.e. the CO₂ diffusion coefficients decrease initially and then increase with the increasing pressure [32].

The results obtained by Yang and Gu [8] are also listed in Table 1 for comparison. The effective diffusion coefficients calculated in this work are the same order of magnitude as those from Yang and Gu [8], i.e. nearly two orders of magnitude larger than the molecular diffusion coefficients of CO₂ in water [33, 34], which proves again that the density-driven natural convection greatly accelerates the mass transfer of CO₂ into the brines.

From Figure 7, it is obvious that the difference between our calculated values of the effective diffusion coefficient and the values from the fitting equation is the largest at a pressure of 4.69 MPa for (a) and 7.53 MPa for (b). To verify the effectiveness of the fitting results from Eq. (18), the concentration profiles of aqueous CO₂ with the calculated effective diffusion coefficient and that from Eq. (18) at pressures of 4.69 MPa and 7.53 MPa were investigated and compared. The comparison (see Figure 8) shows that the concentration profiles of the aqueous CO₂ with distance are very close to each other, which shows the effectiveness of Eq. (18).

4.4 Concentration profile with distance

The concentration profiles of aqueous CO₂ with distance were investigated using the chemical potential gradient model (option 1) and the concentration gradient model [8] (option 2). The results illustrated in Figure 9 show that there is an obvious difference between the results obtained using

Figure 7 The effective diffusion coefficients versus pressure in this work. (a) 300.15 K, ■ calculated values based on experimental kinetics data, — polynomial fit results; (b) 331.15 K, ▲ calculated values based on experimental kinetics data; - - - polynomial fit results.

Table 2 Parameters of Eq. (18) for a polynomial fit of the effective diffusion coefficients determined in this work in terms of pressure

T (K)	C_1	C_2	C_3
300.15	537.04320	-241.46265	34.688315
331.15	1918.1113	-556.46995	46.108093

Figure 8 Concentration distribution of the aqueous CO_2 with distance for the calculated effective diffusion coefficient and that from fitting results at the pressures of 4.69 MPa (a) and 7.53 MPa (b).

Figure 9 Calculated concentration distribution of dissolved CO_2 with distance from the interface. (a) 300.15 K, — Fick's Law [8], - - - this work; (b) 331.15 K, — Fick's Law [8], - - - this work.

these two options. At 300.15 K, the results using option 1 are always lower than those using option 2 [8]. At 331.15 K, the results using option 1 are lower at 6.10 MPa and higher at the other two pressures compared to the results using option 2. This work shows that it is important to consider the non-ideality of the systems in order to obtain reliable results.

4.5 Predicted densities of CO_2 -dissolved brines

The densities of CO_2 -dissolved brines at different times for

Tests 1 to 6 were predicted with the chemical potential gradient model (option 1) and are shown in Figure 10. The densities of the CO_2 -dissolved brine increase with the CO_2 dissolution in brines, and this observation agrees with those from the literature [6, 8, 18]. As the pressure decay resulted from the dissolution of CO_2 in the brine, the densities of the CO_2 -dissolved brines increase with decreasing CO_2 pressure. The results in Figure 10 also show the greater effects of temperature on the densities of the CO_2 -dissolved brine than those of the initial CO_2 pressure.

Figure 10 Predicted density distribution of CO₂-dissolved brines with distance from the interface at different times after $t = 180$ s for Tests 1 to 6 with the chemical potential gradient model and modified Fick's law.

The results using the concentration gradient model (option 2) are also illustrated in Figure 10 for comparison. Again, differences between the results using the two options are observed. For Test 1 the density of the CO₂-dissolved brines with option 1 is higher at 23 s but lower at 662 s than the results with option 2. For Test 2 at 31 and 546 s, the density of the CO₂-dissolved brines using option 1 is lower than those using option 2. For Test 3, the comparison results are similar to those for Test 2, while for Tests 4 and 5, the comparison results are similar to that of Test 1. For Test 6, the density of the CO₂-dissolved brines in option 1 is always higher than those using option 2.

5 Conclusions

The mass transfer of CO₂ in brines at elevated pressures was investigated by means of a chemical potential gradient model based on non-equilibrium thermodynamics, in which SAFT1-RPM EoS was used to calculate the fugacity coefficients of aqueous CO₂ in brines, and the effective diffusion coefficients were obtained from the iterative calculation based on the experimental kinetic data. The density profile was then predicted by the model. The following conclusions can be drawn:

(1) The interfacial concentration of aqueous CO₂ increases with increasing pressure and decreasing temperature. The interfacial densities of CO₂-saturated brines increase with increasing pressure and decreasing temperature, and the effect of pressure on density was below 0.1%.

(2) With increasing pressure the effective diffusion coefficients decrease initially and then increase, with a good fitting of the effective diffusion coefficient in terms of pressure by a polynomial.

(3) Considerably different aqueous CO₂ concentration profiles were obtained with the chemical potential gradient model compared to the concentration gradient model, which shows the importance of considering the non-ideality of the systems in order to obtain reliable results.

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- Bachu S. Sequestration of CO₂ in geological media: Criteria and approach for site selection in response to climate change. *Energy Convers. Manage.*, 2000, 41: 953–970
- Schrag DP. Preparing to capture carbon. *Science*, 2007, 315: 812–813
- Firoozabadi A, Cheng P. Prospects for subsurface CO₂ sequestration. *AIChE J.*, 2010, 56: 1398–1405
- Bruant RG Jr, Guswa AJ, Celia MA, Peters CA. Safe storage of CO₂ in deep saline aquifers. *Environ Sci Technol*, 2002, 36: 240A–245A
- Hassanzadeh H, Pooladi-Darvish M, Keith DW. Accelerating CO₂ dissolution in saline aquifers for geological storage — Mechanistic and sensitivity studies. *Energy Fuels*, 2009, 23: 3328–3336
- Bachu S, Adams JJ. Sequestration of CO₂ in geological media in response to climate change: Capacity of deep saline aquifers to sequester CO₂ in solution. *Energy Convers Manage.*, 2003, 44: 3151–3175
- Michael K, Golab A, Shulakova V, Ennis-King J, Allinson G, Sharma S, Aiken T. Geological storage of CO₂ in saline aquifers — A review of the experience from existing storage operations. *Int J Greenh Gas Con.*, 2010, 4: 659–667
- Yang C, Gu Y. Accelerated mass transfer of CO₂ in reservoir brine due to density-driven natural convection at high pressures and elevated temperatures. *Ind Eng Chem Res*, 2006, 45: 2430–2436
- Gilfillan SMV, Lollar BS, Holland G, Blagburn D, Stevens S, Schoell M, Cassidy M, Ding Z, Zhou Z, Lacrampe-Couloume G, Ballentine CJ. Solubility trapping in formation water as dominant CO₂ sink in natural gas fields. *Nature*, 2009, 458: 614–618
- Keith DW, Giardina JA, Morgan MG, Wilson EJ. Regulating the underground injection of CO₂. *Environ Sci Technol*, 2005, 39: 499A–505A
- Oldenburg CM. Transport in geologic CO₂ storage systems. *Transp Porous Med*, 2010, 82: 1–2
- Weir GJ, White SP, Kissling WM. Reservoir storage and containment of greenhouse gases. *Energy Convers Manage.*, 1995, 36: 531–534
- Teng H, Yamasaki A. Mass transfer of CO₂ through liquid CO₂-water interface. *Int J Heat Mass Transfer*, 1998, 41: 4315–4325
- Ogasawara K, Yamasaki A, Teng H. Mass transfer from CO₂ drops traveling in high-pressure and low-temperature water. *Energy Fuels*, 2001, 15: 147–150
- Arendt B, Dittmar D, Eggers R. Interaction of interfacial convection and mass transfer effects in the system CO₂-water. *Int J Heat Mass Transfer*, 2004, 47: 3649–3657
- Farajzadeh R, Salimi H, Zitha PLJ, Bruining H. Numerical simulation of density-driven natural convection in porous media with application for CO₂ injection projects. *Int J Heat Mass Transfer*, 2007, 50: 5054–5064
- Farajzadeh R, Barati A, Delil HA, Bruining J, Zitha PLJ. Mass transfer of CO₂ into water and surfactant solutions. *Pet Sci Technol*, 2007, 25: 1493–1511
- Farajzadeh R, Zitha PLJ, Bruining J. Enhanced mass transfer of CO₂ into water: Experiment and modeling. *Ind Eng Chem Res*, 2009, 48: 6423–6431
- Kneafsey TJ, Pruess K. Laboratory flow experiments for visualizing carbon dioxide-induced, density-driven brine convection. *Transp Porous Med*, 2010, 82: 123–139
- Kocherginsky N, Zhang YK. Role of standard chemical potential in transport through anisotropic media and asymmetrical membranes. *J Phys Chem B*, 2003, 107: 7830–7837
- Liu C, Ji Y, Shao Q, Feng X, Lu X. Thermodynamic analysis for synthesis of advanced materials. Molecular thermodynamics of complex systems. *Struct Bond*, 2009, 131: 193–270
- Ji YH, Ji XY, Liu C, Feng X, Lu XH. Modelling of mass transfer coupling with crystallization kinetics in microscale. *Chem Eng Sci*, 2010, 65: 2649–2655
- Lu XH, Ji YH, Liu HL. Non-equilibrium thermodynamics analysis and its application in interfacial mass transfer. *Sci China Chem*, 2011, 54: 1659–1666
- Ji XY, Tan SP, Adidharma H, Radosz M. SAFT1-RPM approximation extended to phase equilibria and densities of CO₂-H₂O and CO₂-H₂O-NaCl systems. *Ind Eng Chem Res*, 2005, 44: 8419–8427
- Ji YH, Ji XY, Feng X, Liu C, Lu LH, Lu XH. Progress in the study on the phase equilibria of the CO₂-H₂O and CO₂-H₂O-NaCl systems. *Chin J Chem Eng*, 2007, 15: 439–448
- Adidharma H, Radosz M. Prototype of an engineering equation of state for heterosegmented polymers. *Ind Eng Chem Res*, 1998, 37: 4453–4462
- Adidharma H, Radosz M. Square-well SAFT equation of state for homopolymeric and heteropolymeric fluids. *Fluid Phase Equilib*, 1999, 158: 165–174
- Tan SP, Adidharma H, Radosz M. Statistical associating fluid theory coupled with restricted primitive model to represent aqueous strong electrolytes. *Ind Eng Chem Res*, 2005, 44: 4442–4452
- Ji XY, Tan SP, Adidharma H, Radosz M. Statistical associating fluid theory coupled with restricted primitive model to represent aqueous strong electrolytes: Multiple-salt solutions. *Ind Eng Chem Res*, 2005, 44: 7584–7590
- Prausnitz JM, Lichtenthaler RN, de Azevedo EG. *Molecular Thermodynamics of Fluid-phase Equilibria (3rd edition)*. New Jersey: Prentice Hall PTR, 1999
- Crank J. *The Mathematics of Diffusion (2nd edition)*. Oxford: Clarendon Press, 1975
- Tewes F, Boury F. Formation and rheological properties of the supercritical CO₂-water pure interface. *J Phys Chem B*, 2005, 109: 3990–3997
- Frank MJW, Kuipers JAM, van Swaaij WPM. Diffusion coefficients and viscosities of CO₂ + H₂O, CO₂ + CH₃OH, NH₃ + H₂O, and NH₃ + CH₃OH liquid mixtures. *J Chem Eng Data*, 1996, 41: 297–302
- Rowley RL, Adams ME, Marshall TL, Oscarson JL, Wilding WV, Anderson DJ. Measurement of diffusion coefficients important in modeling the absorption rate of carbon dioxide into aqueous N-methyldiethanolamine. *J Chem Eng Data*, 1997, 42: 310–317