A model for single-phase \( \text{PVTx} \) properties of \( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O}-\text{NaCl} \) fluid mixtures from 273 to 1273 K and from 1 to 5000 bar

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Abstract

A thermodynamic model explicit in Helmholtz free energy is constructed to calculate the single-phase \( \text{PVTx} \) properties of the \( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O}-\text{NaCl} \) fluid mixtures. Parameters of the binary \( \text{CO}_2-\text{H}_2\text{O}, \text{CH}_4-\text{H}_2\text{O}, \text{C}_2\text{H}_6-\text{H}_2\text{O} \) and \( \text{N}_2-\text{H}_2\text{O} \) mixtures are regressed from assessed experimental data. On the basis of the binary mixture parameters, the model can be used to predict the single-phase volumes of the \( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O}-\text{NaCl} \) fluid mixtures with a simple approach. Comparison with a large number of experimental data shows that the model can reproduce the single-phase \( \text{PVTx} \) properties of the \( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O}-\text{NaCl} \) fluid mixtures from 273 to 1273 K and from 1 to 5000 bar, with or close to experimental accuracy. Online calculations can be made on the website: www.geochem-model.org/.

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1. Introduction

\( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O}-\text{NaCl} \) mixtures are typical geological fluids in the Earth's crust. Thermodynamic properties of the mixtures, especially vapor–liquid phase equilibria \( (\text{Duan et al., 1995; Duan and Sun, 2003; Mao et al., 2005; Duan and Mao, 2006; Mao and Duan, 2006}) \) and pressure–volume–temperature–composition \( (\text{PVTx}) \) properties \( (\text{Bakker, 1999; Duan et al., 1996, 2003; Mao and Duan, 2008}) \), are fundamental in the quantitative interpretation of boiling, immiscibility, gas solubility, and fluid migration, and also in the studies of fluid inclusions \( (\text{Diamond, 2001; Dubessy et al., 1999, 2001; Guillaume et al., 2003; Vasyukova and Fonarev, 2006}) \). Due to highly non-ideal mixing properties of the gas–\( \text{H}_2\text{O}-\text{NaCl} \) fluid mixtures, it is difficult to predict both the phase equilibria and volumetric properties simultaneously with a single equation of state within experimental uncertainty over a large temperature–pressure–composition region, such as 273–1273 K, 1–5000 bar and 0–1 \( \text{NaCl} \) (mole fraction of \( \text{NaCl} \)). However, it is possible to use an equation of state to calculate the volume of the gas–\( \text{H}_2\text{O}-\text{NaCl} \) mixtures, and use another model to predict the vapor–liquid phase equilibria. The main interest of the paper is to predict the molar volume of the \( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O}-\text{NaCl} \) fluid mixtures, from which homogenization volume (or density) and isochores can be obtained in the studies of the fluid inclusions.

Previously, \text{Lemmon and Jacobsen (1999)} \) developed a generalized equation of state explicit in Helmholtz free energy to predict the thermodynamic properties of mixtures containing \( \text{CH}_4, \text{C}_2\text{H}_6, \text{n-C}_4\text{H}_{10}, \text{i-C}_4\text{H}_{10}, \text{C}_2\text{H}_4, \text{N}_2, \text{Ar}, \text{O}_2 \) and \( \text{CO}_2 \) within the estimated accuracy of experimental data. In that model, equations of state of pure fluid are from those \text{NIST} \) recommends. However, \( \text{H}_2\text{O} \), as one of important natural fluids, is not included in that model. Several years later, \text{Paulus and Penoncello (2006)} \) extended the generalized model \( (\text{Lemmon and Jacobsen, 1999}) \) to calculate the single-phase thermodynamic properties of \( \text{CO}_2-\text{H}_2\text{O} \) mixture. However, this model has systematic volumetric deviations at low temperatures by comparison to experimental volumetric data, as discussed below. Recently, \text{Driesner (2007)} \) presented a volumetric correlation for \( \text{NaCl}-\text{H}_2\text{O} \) fluid covering a large temperature–pressure–composition region of 273–1273 K, 0–5000 bar and 0–1 \( \text{NaCl} \) (mole fraction of \( \text{NaCl} \)). However, a volumetric model of the multi-component gas–water–salt fluid mixtures like the \( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O}-\text{NaCl} \) from 273 to 1273 K and pressures up to 5000 bar is still lacking.

In this study, the generalized equation of state \( (\text{Lemmon and Jacobsen, 1999}) \) is extended to calculate the volume of the \( \text{CO}_2-\text{CH}_4-\text{C}_2\text{H}_6-\text{N}_2-\text{H}_2\text{O} \) mixtures, and new parameters for the binary \( \text{CO}_2-\text{H}_2\text{O}, \text{CH}_4-\text{H}_2\text{O}, \text{C}_2\text{H}_6-\text{H}_2\text{O} \) and \( \text{N}_2-\text{H}_2\text{O} \) mixtures are evaluated. Combining
Table 1
Experimental measurements for the volumetric properties of the binary CO₂-H₂O, CH₄-H₂O, C₂H₆-H₂O and N₂-H₂O fluid mixtures.

Table 2
Coefficients and exponents of mixture Eq. (4).

Table 3
Critical parameters of pure fluids.

Note: T, P, and x refer to temperature, pressure, and mole fraction, respectively, so is the same in Tables 5-6; Nd: Number of measurements.

Data are from molecular simulation.

the volumetric models of the NaCl-H₂O (Driesner, 2007) and CO₂-CH₄-C₂H₆-N₂-H₂O fluid mixtures with a simple method, the model can be used to predict the single-phase molar volume of the CO₂-CH₄-
2. Volumetric model for the CO$_2$–C$_2$H$_6$–N$_2$–H$_2$O fluid mixtures

2.1. Review of experimental volumetric data

On the experimental volumetric data of CO$_2$–C$_2$H$_6$–N$_2$–H$_2$O fluid mixtures, detailed review can be seen from the study of Kunz et al. (2007). Here we focus on the experimental volumetric data of the binary aqueous systems: CO$_2$–H$_2$O, CH$_4$–H$_2$O, C$_2$H$_6$–H$_2$O and N$_2$–H$_2$O (Table 1).

2.1.1. CO$_2$–H$_2$O system

From Table 1, it can be seen that there are many experimental volumetric measurements on the CO$_2$–H$_2$O fluid mixtures. Over 3500 data points have been reported for this system, covering a large T–P–x$_{CO2}$ range from 273 to 1673 K, 1 to 19,400 bar and 0 to 1x$_{CO2}$. Most data are consistent with each other. Experimental precision is about 0.1–
0.5% below 647 K, above which experimental uncertainties increase to 1%. Hu et al. (2007) reviewed in detail the volumetric data of the binary system up to 647 K. It should be pointed out that the volumetric data of Nighswander et al. (1989) and Teng et al. (1997) below 647 K have large uncertainties. Above 647 K, data of Franck and Tödheide (1959) are inconsistent with others’ experimental measurements at the same T–P–xCO2 range, with about average deviation of 4% from others. The data of Brodholt and Wood (1993) and Duan and Zhang (2006) are from molecular-dynamics simulation and cover a very large T–P–xCO2 space. All volumetric data listed in Table 1 but those (Franck and Tödheide, 1959; Nighswander et al., 1989; Brodholt and Wood, 1993; Frost and Wood, 1997; Teng et al., 1997; Duan and Zhang, 2006) are used in the parameterization. The data of Duan and Zhang (2006) and Frost and Wood (1997) at high temperatures and pressures are not used in the parameterization but as a test of the extrapolation ability of the volumetric model.

2.1.2. CH4–H2O system

Experimental volumetric data sets for the CH4–H2O fluid mixture are also listed in Table 1. The data of Welsch (1973) and Christotoforakos (1985) are in form of graphs and are not included in the parameterization. The data (Joffrion and Eubank, 1988, 1989; Fenghour et al., 1996b; Hnedkovsky et al., 1996) are of high accuracy. The data of Zhang et al. (2007) are from molecular simulation and cover a large T–P–xCH4 region. The PVTx data near critical region are difficult to measure and contain large uncertainties. The data of Shmonov et al. (1993) at 1400 bar have a very large deviation. We compared the data to equation of state of pure CH4 (Setzmann and Wagner, 1991), and found that the deviation is over 8% at 1400 bar. Hence the data at 1400 bar are corrected according to the equation of state of pure CH4 (Setzmann and Wagner, 1991). The experimental volumetric data (Sretenskaya et al., 1986; Joffrion and Eubank, 1988, 1989; Abdulagatov et al., 1993a,b; Hnedkovsky et al., 1996; Shmonov et al., 1993; Fenghour et al., 1996b; Hnedkovsky et al., 1996; Zhang, 1997) are used in the parameterization. The data of Zhang et al. (2007) are not used in the parameterization but as a test of extrapolation ability of the volumetric model.

2.1.3. C2H6–H2O system

Only one experimental volumetric data set (Lancaster and Wormald, 1987) is found for the C2H6–H2O mixtures up to 773.2 K and 120 bar. Therefore, these data points (115) are used in the parameterization of the model. Apparently, future experimental measurements are needed for this binary system.

2.1.4. N2–H2O system

Experimental volumetric data of the N2–H2O system (Japas and Frank, 1985; Abdulagatov et al., 1993a; Fenghour et al., 1993) are not as extensive as those of the CO2–H2O and CH4–H2O fluid mixtures. These experimental data cover a T–P–xN2 range of 429–698 K, 21–2775 bar and 0.1–0.95, and are consistent with each other, so they are all used in the parameterization.

2.1.5. Ternary systems

Two experimental data sets of CH4–C2H6–CO2 fluid mixtures (Hou et al., 1996; McElroy et al., 2001) and one experimental data set of CH4–CO2–N2 mixtures (Seitz and Blencoe, 1996) have been found in literature. These data will be used as a test of the model predictability in Section 2.3. For CO2–CH4–H2O mixture and other multi-component systems, no PVTx data are found and experimental measurements are needed for the test of the model.

2.2. Volumetric model in Helmholtz free energy

The volumetric model of the CO2–CH4–C2H6–N2–H2O fluid mixtures is in terms of dimensionless Helmholtz free energy α, defined as

\[
\alpha = \frac{A}{RT}
\]

where A is molar Helmholtz free energy, R is molar gas constant whose value is 8.314472 J mol⁻¹ K⁻¹, and T denotes temperature in K. So are the same in the following equations.
The dimensionless Helmholtz free energy \( \alpha \) of the mixture is represented by

\[
\alpha = \alpha_{\text{id}}^m + \alpha^E
\]

where \( \alpha_{\text{id}}^m \) is the dimensionless Helmholtz free energy of an ideal mixture and \( \alpha^E \) is the excess dimensionless Helmholtz free energy. \( \alpha_{\text{id}}^m \) comes directly from the fundamental equations of pure fluids and can be written as

\[
\alpha_{\text{id}}^m = \alpha_{\text{id}}^0(\delta, \tau, \chi) + \sum_{i=1}^{n} x_i \alpha_i^r(\delta, \tau)
\]

where \( \alpha_{\text{id}}^0 \) is an ideal-gas part of dimensionless Helmholtz free energy of the mixture, \( \alpha_i^r \) is the ideal-gas part of dimensionless Helmholtz free energy of component \( i \), \( \alpha_i^r \) is a residual part of dimensionless Helmholtz free energy of component \( i \), \( x_i \) is mole fraction of the component \( i \). \( \text{id} \) in superscript denotes ideal mixing, \( \delta \) and \( \tau \) in the superscripts denote the ideal-gas part and the residual part of dimensionless Helmholtz free energy, respectively. \( i \) and \( m \) in subscripts denote the component and mixtures, respectively. \( \delta \) and \( \tau \) are reduced parameters, which are defined by

\[
\delta = \frac{\rho}{\rho_c}
\]

\[
\tau = \frac{T}{T_c}
\]

where \( \rho \) is the density of the mixtures, and \( \rho_c \) and \( T_c \) are defined as

\[
\rho_c = \left[ \frac{\sum_{i=1}^{n} x_i \rho_{ci}}{\sum_{i=1}^{n} x_i} \right]^{-1}
\]

\[
T_c = \sum_{i=1}^{n} x_i T_{ci} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \frac{\rho_{ci} S_{ij}}{\rho_{cj} S_{ij}}
\]

where \( \rho_{ci} \) and \( T_{ci} \) are the critical density and critical temperature of the component \( i \), respectively. \( x_i \) denotes mole fraction of the component.

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**Fig. 4.** Volumetric deviations of CH₄–H₂O mixtures in high temperature–pressure region.

**Fig. 5.** Volumetric deviations of this model from experimental data for C₂H₆–H₂O fluid mixtures.

**Fig. 6.** Volumetric deviations of this model from experimental data for N₂–H₂O fluid mixtures.
Values of the binary parameters ($\zeta_{ij}$, $\eta_i$, $\beta_i$, and $F_i$) in the above equations for the CO$_2$--CH$_4$--C$_2$H$_6$--N$_2$ mixtures are from the model (Lemmon and Jacobsen, 1999), and the parameter values of the binary CO$_2$--H$_2$O, CH$_4$--H$_2$O, C$_2$H$_6$--H$_2$O and N$_2$--H$_2$O mixtures are determined by a regression to experimental volumetric data analyzed above. In this article, equations of state for pure CO$_2$, CH$_4$, C$_2$H$_6$, N$_2$ and H$_2$O fluids are from references (Setzmann and Wagner, 1991; Span and Wagner, 1996; Span et al., 2000; Wagner and Prüß, 2002; Bucker and Wagner, 2006). These equations of state are all explicit in dimensionless Helmholtz energy and are considered the best equations of these pure fluids. Critical parameters of the pure CO$_2$, CH$_4$, C$_2$H$_6$, N$_2$ and H$_2$O fluids are listed in Table 3.

2.3. Parameterization and comparisons

As mentioned above, the values of $\zeta_{ij}$, $\eta_i$, $\beta_i$ and $F_i$ for the CO$_2$--H$_2$O, CH$_4$--H$_2$O, C$_2$H$_6$--H$_2$O and N$_2$--H$_2$O mixtures are determined by a nonlinear regression to experimental volumetric data. Regressed parameter values of the CO$_2$--H$_2$O, CH$_4$--H$_2$O, C$_2$H$_6$--H$_2$O and N$_2$--H$_2$O mixtures and those of the CO$_2$--CH$_4$--C$_2$H$_6$--N$_2$ mixtures are listed in Table 4. The molar volume of the CO$_2$--CH$_4$--C$_2$H$_6$--N$_2$--H$_2$O mixtures can be calculated from Eq. (9) with the Newton iterative method. If the CO$_2$--CH$_4$--C$_2$H$_6$--N$_2$--H$_2$O fluid mixtures are in vapor or supercritical state, we can set the initial value of density for that of ideal gas. If the CO$_2$--CH$_4$--C$_2$H$_6$--N$_2$--H$_2$O fluid mixtures are in liquid state, saturated liquid density value of the pure component with the highest critical temperature can be set as the initial density value.

$$P = \rho RT \left[ 1 + \delta \left( \frac{\partial \alpha^p}{\partial \tau} \right) \right]$$

where $P$ is pressure, and $\alpha^p = \sum_{i=1}^{n} x_i \alpha^p(i, \tau) + \alpha^p(\delta, \tau, x_i)$.

With the above parameters, the molar volumes of the CO$_2$--H$_2$O, CH$_4$--H$_2$O, C$_2$H$_6$--H$_2$O and N$_2$--H$_2$O mixtures can be calculated. Table 5 shows the average and maximum absolute deviations of the model from each data set. Fig. 1 shows the comparisons between experimental results and model predictions for the CO$_2$--H$_2$O system at low temperatures. It can be seen in Fig. 1 that the molar volumes calculated from the parameters of the model (Paulus and Penoncello, 2006) have systematic negative deviations. In order to test the model predictive ability, we compared the model to the data (Frost and Wood, 1997; Duan and Zhang, 2006) up to 1673 K and 19,400 bar (Fig. 2), which shows average absolute deviation of about 2%, indicating the good extrapolation ability of the model. Figs. 3–4 show the volumetric deviations from experimental data for the CH$_4$--H$_2$O mixtures. Figs. 5–6 show the volumetric deviations from experimental data for the C$_2$H$_6$--H$_2$O and N$_2$--H$_2$O mixtures, respectively. For the CH$_4$--H$_2$O and N$_2$--H$_2$O mixture, some deviations from experimental data near the critical regions are very large, where experimental measurements are difficult to do and volumetric data in themselves contain large uncertainties. So the model prediction is also poor in these regions. In addition, experimental volumetric data of the CH$_4$--C$_2$H$_6$--CO$_2$ (Hou et al., 1996; McElroy et al., 2001) (Fig. 7) and CH$_4$--CO$_2$--N$_2$ (Seitz and Blencoe, 1996) (Fig. 8) mixtures are also compared, which show good agreement. As seen from these figures, the molar volume of the CO$_2$--CH$_4$--C$_2$H$_6$--N$_2$--H$_2$O mixtures up to 1273 K and 10,000 bar can be reproduced by this generalized model within or near experimental uncertainties.

In the study of fluid inclusions, isochors are important for obtaining the temperature and pressure of fluids trapped in minerals, which can be calculated from above model. Figs. 9–11 show the calculated isochors of the CO$_2$--H$_2$O, CH$_4$--H$_2$O and CH$_4$--CO$_2$ systems, respectively. From Figs. 9–10, it can be seen that the isochors of the CO$_2$--H$_2$O and CH$_4$--H$_2$O mixtures at low temperatures are a bit curved and almost linear in other regions. Experimental isochors of the CO$_2$--
H2O mixture (Sterner and Bodnar, 1991) are compared in Fig. 9a,b. It can be seen that the experimental isochores, whose valid temperature–pressure–composition range is 673–973 K, 2000–6000 bar, and 0–1 mole fraction of CO2 are in good agreement with our calculated results. The iso-Th lines, which can be approximated as isochores, reported by Lin and Bodnar (2010) for the CH4–H2O mixture are also plotted for comparison in Fig. 10a,b. The experimental equation of iso-Th lines is valid from the bubble point to 773 K, 3000 bar and compositions ≤4 mol% CH4. It can be seen from Fig. 10a, b that the calculated isochores from this study are quite close to the iso-Th lines. From Fig. 11, it can be seen that the isochores of the CH4–CO2 mixture from 273 to 1273 K are curved similar to those of pure CO2 fluid.


CO2–H2O–NaCl and CH4–H2O–NaCl are the most frequently encountered gas–water–salt natural systems. However, up to now, no a volumetric model of the gas–H2O–NaCl mixtures is valid for the T–P–xNaCl region of 273–1273 K, 1–5000 bar and 0–1 xNaCl. When the gas–H2O–NaCl mixtures are in vapor state, NaCl content is very small. Hence, the fluids can be approximated as salt-free mixtures, and the molar volume can be calculated from above equations. When the gas–H2O–NaCl mixtures are in liquid or in supercritical state, the molar volume is obtained from the following equation:

\[
V = x_{\text{H}_2\text{O}\text{NaCl}} V_{\text{H}_2\text{O}\text{NaCl}} + x_{\text{gas}} V_{\text{gas,0}}
\]  

where \(V\) is molar volume of the gas–H2O–NaCl fluid mixtures, \(V_{\text{H}_2\text{O}\text{NaCl}}\) is the molar volume of the binary H2O–NaCl solution calculated from the model (Driesner, 2007), \(x_{\text{H}_2\text{O}\text{NaCl}}\) denotes the mole fraction of the H2O–NaCl components, \(x_{\text{gas}}\) denotes the mole fraction of gas (pure CO2, CH4, C2H6, N2 or their mixtures) in gas–H2O–NaCl fluids, and \(V_{\text{gas,0}}\) refers to apparent molar volume of gas in the H2O–NaCl fluids.

Usually, gas (CO2, CH4, C2H6, N2) solubility in water is not big. If NaCl is added, the gas solubility will decrease rapidly with increasing salinity. Therefore, the possibilities of gas–Na+ and gas–Cl− pairs appearing in fluids are very small. In this case, the effect of NaCl on \(V_{\text{gas,0}}\) can be neglected. That is, \(V_{\text{gas,0}}\) can be approximated as the apparent molar volume of the gas in water (\(\frac{\phi_{\text{gas,0}}}{V}\)). Eq. (10) is then changed for

\[
V = x_{\text{H}_2\text{O}\text{NaCl}} V_{\text{H}_2\text{O}\text{NaCl}} + x_{\text{gas}} \frac{\phi_{\text{gas,0}}}{V_{\text{gas,0}}}
\]  

where \(\frac{\phi_{\text{gas,0}}}{V_{\text{gas,0}}}\) is calculated from the above salt-free PVTx model. For the CO2–H2O–NaCl mixture where \(x_{\text{CO2}}=0.05\), the approximation proves to be very good below 647 K (Duan et al., 2008). In order to test the validity of Eq. (11), the experimental single-phase volume data of the CO2–H2O–NaCl mixture (Gehrig et al., 1986; Nighswander et al., 1989; Johnson, 1992; Schmidt et al., 1995; Teng and Yamasaki, 1998; Li et al., 2004; Song et al., 2005) are compared with the model. Table 6 lists the average and maximum absolute deviations and Fig. 12 shows the volumetric deviations of Eq. (11) from experimental data of the CO2–H2O–NaCl mixtures. It can be seen from Table 6 and Fig. 12 that the agreement is excellent. Fig. 13 shows that the experimental single-phase...
phase volume data of the CH$_4$–H$_2$O–NaCl fluid mixture (Krader and Franck, 1987) at 800 K are also in good agreement with the model. However, when compared to the saturated density of the CO$_2$–H$_2$O–NaCl (Gehrig et al., 1986), CH$_4$–H$_2$O–NaCl (Krader and Franck, 1987) and C$_2$H$_6$–H$_2$O–NaCl (Michelberger and Franck, 1990) mixtures, large deviations are found. For example, the average absolute deviation of the saturated experimental density data (total 138 data points) is 3.85% for the CH$_4$–H$_2$O–NaCl system (Krader and Franck, 1987).

Therefore, Eq. (11) can only be used to predict the single-phase volume of the gas–H$_2$O–NaCl fluid mixtures. Fig. 14 shows the isochores and the lines of equal homogenization temperature at constant compositions (Schmidt and Bodnar, 2000) for the CO$_2$–H$_2$O–NaCl fluid mixtures. Apparently, the results from Eq. (11) deviate significantly from those of Schmidt and Bodnar (2000) in some regions. Therefore, the isochores calculated from Eq. (11) may be only used as an approximation in these regions, but the trend of the isochores is correct. Because no experimental volumetric data of other single-phase gas–H$_2$O–NaCl mixtures have been found, future experimental work for those mixtures is needed to further validate Eq. (11).

Limitation of the model: The above discussion suggests that although the model extrapolates well, we should pay attention to the applicable range of the model. For the CO$_2$–CH$_4$–C$_2$H$_6$–N$_2$–H$_2$O mixtures, it can be safely used to calculate the single-phase molar volumes in the temperature–pressure region that equation of state of pure fluids cover, beyond which it can be used up to 1273 K and 10,000 bar with slightly lower accuracy. For the CO$_2$–CH$_4$–C$_2$H$_6$–N$_2$–H$_2$O–NaCl mixtures, it can only be used to calculate the single-phase PVTx properties of gas–H$_2$O–NaCl mixtures from 273 to 1273 K and pressures to 5000 bar.

4. Conclusions

A generalized thermodynamic mixture model based on Helmholtz free energy proposed by Lemmon and Jacobsen (1999) is extended to calculate the molar volume of the CO$_2$–CH$_4$–C$_2$H$_6$–N$_2$–H$_2$O fluid mixtures. With a simple approximate method, the model can be used to predict the single-phase volumes or densities of the CO$_2$–CH$_4$–C$_2$H$_6$–N$_2$–H$_2$O–NaCl fluid mixtures. It shows that the model can reproduce the volume of the CO$_2$–CH$_4$–C$_2$H$_6$–N$_2$–H$_2$O–NaCl fluid mixtures from 273 to 1273 K and from 1 to 5000 bar with or close to experimental accuracy. The model for the CO$_2$–CH$_4$–C$_2$H$_6$–N$_2$–H$_2$O–NaCl fluid mixtures established here is very useful for calculating the isochores of the corresponding gas–water–salt fluid inclusions.

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Volumetric deviations from experimental data for CO₂–H₂O fluid mixture

Table 6

<table>
<thead>
<tr>
<th>References</th>
<th>T (K)</th>
<th>P (bar)</th>
<th>x₂CO₂</th>
<th>x₃NaCl</th>
<th>Nd</th>
<th>AAD (%)</th>
<th>MAD (%)</th>
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<td>Gehrig et al. (1986)</td>
<td>673–773</td>
<td>400–3900</td>
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<td>353.35–473.65</td>
<td>21.1–100.3</td>
<td>0.0029–0.0154</td>
<td>0.003</td>
<td>34</td>
<td>0.90</td>
<td>2.83</td>
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<tr>
<td>Johnson (1992)</td>
<td>1197.15–1213.15</td>
<td>6600–7458</td>
<td>0.187–0.489</td>
<td>0.0244–0.0617</td>
<td>4</td>
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<td>2.82</td>
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<td>623.15–973.15</td>
<td>2000–4000</td>
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<td>0.1633</td>
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<td>278–293</td>
<td>64.4–294.9</td>
<td>0.0232–0.0322</td>
<td>0.0106</td>
<td>24</td>
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<td>37</td>
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<td>Song et al. (2005)</td>
<td>2761.25–2831.5</td>
<td>40–130</td>
<td>0.00422–0.01352</td>
<td>0.011</td>
<td>90</td>
<td>0.21</td>
<td>0.25</td>
</tr>
</tbody>
</table>

AAD: Average absolute deviations calculated from this model; MAD: Maximum absolute deviations calculated from this model; Nd: Number of data points.


Lancaster, N.M., Wormald, C.J., 1987. The excess molar enthalpies of (0.5H2O+0.5C2H4)(g) and (0.5H2O+0.5C2H6)(g) at high temperatures and pressures. The Journal of Chemical Thermodynamics 19 (1), 89–97.


Fig. 12. Volumetric deviations of this model from experimental data for CO2–H2O–NaCl fluid mixtures.
Lin, F., Bodnar, R.J., 2010. Synthetic fluid inclusions XVIII: experimental determination of the PVTX properties of H_2O–CH_4 to 500 °C, 3 kbar and X_{CH_4} ≤ 4 mol.%. Geochimica et Cosmochimica Acta 74 (11), 3260–3273.


Fig. 13. Comparisons with experimental volumetric data of CH_4–H_2O–NaCl mixtures.

Fig. 14. Isochores and lines of equal homogenization temperature at constant compositions for the CO_2–H_2O–NaCl fluid mixtures: L–V curve denotes liquid–vapor curve.