Phase equilibria of CO_2 hydrate in NaCl–$MgCl_2$ aqueous solutions

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ABSTRACT

Phase equilibrium data for CO_2 hydrate in presence of binary NaCl–$MgCl_2$ aqueous solutions were obtained at four different concentrations (2 wt%NaCl–8 wt%$MgCl_2$, 8 wt%NaCl–2 wt%$MgCl_2$, 5 wt% NaCl–15 wt%$MgCl_2$, 15 wt% NaCl–5 wt%$MgCl_2$) in the temperature range of (258.63 to 276.45) K and in the pressure range of (1.34 to 3.41) MPa, respectively. The measurements were carried out by employing isochoric pressure search method with uncertainties of ±0.1 K for temperature and ±0.02 MPa for pressure. The hydrate equilibrium data for the (CO_2 + water) system were compared with some experimental data from the literature, and the acceptable agreement demonstrated the reliability of the experimental method used in this work. The van der Waals and Platteeuw (vdW–P) solid solution theory was used to model the hydrate phase, and the equation of Weiss combined with Pitzer-based model was applied to characterize the activity of water. The predicted results were in good consistency with the experimental data, and the average pressure deviation was 5.13%.

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1. Introduction

Gas hydrates are ice-like inclusion compounds composed primarily of a hydrogen bond network of water molecules trapping small guest molecules (e.g., methane, ethane, propane, etc.) [1,2]. There are mainly three kinds of gas hydrates, structures I, II, and H [3]. Carbon dioxide hydrate is structure I hydrate with a chemical formula of $8CO_2 \cdot 46H_2O$ if all cavities are occupied [4].

The global greenhouse effect of CO_2 has aroused much attention among the public. Ideas for CO_2 disposal in the ocean [5] and CO_2 storage on the ocean floor [6–8] have been proposed as the possible ways to reduce CO_2 emission [9,10]. In both proposals, carbon dioxide hydrate would play an important role in preventing deep sea sequestered CO_2 from going back to the atmosphere. Ohgaki et al. [11] suggested exploiting natural gas hydrate with carbon dioxide. It combined CH_4 production and CO_2 sequestration. And the formation heat of CO_2 hydrate met the heat demanded to decompose CH_4 hydrate. The formation of carbon dioxide hydrate reduced the submarine geological structure damage in natural gas hydrate exploitation process. Electrolytes inhibited the formation of hydrate. This fact meant that the lower temperature and higher pressure conditions in electrolytes aqueous solutions than in pure water were needed to form hydrate [12–14]. Electrolytes in seawater inhibited the formation of CO_2 hydrate, thus the phase equilibrium conditions of CO_2 hydrate in existence of electrolytes aqueous solutions were needed.

Equilibrium conditions of carbon dioxide hydrate in pure water have been reported by many researchers [15–19]. Experimental equilibrium data for carbon dioxide hydrate in electrolytes aqueous solutions have been partly reported. Dholabhai et al. [20] first published the phase equilibrium data of carbon dioxide hydrate in aqueous solutions of NaCl, KCl, $CaCl_2$ and their binary mixtures. Kang et al. [21] reported the equilibrium conditions of carbon dioxide hydrate in $MgCl_2$ aqueous solutions at low concentrations. Clarke et al. [22] investigated the phase equilibrium conditions of carbon dioxide hydrate in the presence of KNO_3, $MgSO_4$, and $CuSO_4$ aqueous solutions. Experimental equilibrium data for methane, ethane and (methane + ethane) mixture hydrate in aqueous solutions of $MgCl_2$ or binary electrolytes which contain $MgCl_2$ have been partly published [23–25]. Javanmardi et al. [26,27] have predicted gas hydrate forming conditions in aqueous mixed-electrolyte solutions. But there were no experimental equilibrium data for carbon dioxide hydrate in the presence of binary electrolytes aqueous solutions which contained $MgCl_2$. The present study reported the experimental and predicted three phase (aqueous solution + vapor + hydrate) equilibrium data of carbon dioxide hydrate in pure water and binary NaCl–$MgCl_2$ aqueous solutions. The predictive values were calculated by the thermodynamic model.

2. Thermodynamic model

When three phase (hydrate + liquid + gas) system is in equilibrium:

$$\mu_w^H = \mu_w^\alpha, \qquad (1)$$

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where μ_w^H and μ_w^α are respectively the chemical potential of water in the hydrate phase and liquid phase. If the chemical potential of hypothetical empty hydrate phase is denoted by μ_w^β, equation (1) can be rewritten as:

$$\mu_w^{\beta-H} = \mu_w^{\beta-\alpha}, \qquad (2)$$

where $\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H$, $\mu_w^{\beta-\alpha} = \mu_w^\beta - \mu_w^\alpha$. $\mu_w^{\beta-H}$ was given according to the van der Waals–Platteeuw model [28], the parameters in this model were calculated according to the work of Parrish and Prausnit [29]. $\mu_w^{\beta-\alpha}$ was given by Holder et al. [30]. The water activity in this model was calculated as follows.

Nasrifar and Moshfeghian [31] derived a simple equation for aqueous solutions containing electrolytes and gas, the activity of water was calculated from equation (3).

$$a_w = a_{w,el} \times a_{w,gas} \qquad (3)$$

$a_{w,el}$ was the activity of water, if the solutions only contained water and electrolytes. $a_{w,el}$ was given by Nasrifar and Moshfeghian [32]:

$$\ln a_{w,el} = \sum_1^{ns} v_i m_i \ln a_{w,el,i}^0 \Big/ \sum_1^{ns} v_i m_i, \qquad (4)$$

where v_i was the stoichiometric number of moles of ions in electrolyte i, m_i was the molality of electrolyte i in the mixed electrolytes aqueous solutions and $a_{w,el,i}^0$ was the activity of water in a single electrolyte aqueous solution containing electrolyte i. The molality of the electrolyte i in the single electrolyte aqueous solution m_i^0 was calculated from the equation (5).

$$m_i^0 = \frac{1}{v_i} \sum_1^{ns} v_j m_j \qquad (5)$$

$a_{w,el,i}^0$ was calculated from the equation (6) given by Pitzer and Mayorga [33].

$$\ln a_{w,el,i}^0 = -18 v_i m_i^0 (1 + z_+ z_- \theta_1 + m_i^0 \theta_2 + m_i^{02} \beta_2)/1000, \qquad (6)$$

where $\theta_1 = -\frac{A_\phi^{0.5}}{1+1.2I^{0.5}}$, $\theta_2 = \beta_0 + \beta_1 e^{-2I^{0.5}}$, m_i^0 was molality, and z was the charge of ion. The parameters β_0, β_1, and β_2 were given by Pitzer and Mayorga [33].

The activity of water which only contained CO_2 was altered by the amount of dissolved gas. It was calculated from equation (7) [34].

$$a_{w,CO_2} \cong x_w = 1 - x_{CO_2}$$
$$= 1 - K_0 f_{CO_2} \exp[(1-P) * v_{CO_2}/RT]/(1+1000/18). \qquad (7)$$

The constant K_0 equaled $\beta/\rho V$ in gravimetric units (mol/kg · atm). It was notable that the units of fugacity and pressure should be atm. The expression of K_0 was:

$$\ln K_0 = A_1 + A_2(100/T) + A_3 \ln(T/100). \qquad (8)$$

The constants A_1, A_2 and A_3 and v_{CO_2} were given by Weiss [34].

3. Experimental

3.1. Materials preparation

The supplier and purity of chemicals used in present study were listed in table 1. Sodium chloride and magnesium chloride were used without any further purification. The deionized water was made in the laboratory, the resistivity of which was 18 MΩ. The magnesium chloride hexahydrate is easy to absorb moisture. The following steps were done to reduce the moisture absorption in the aqueous solution preparation process. First, the entire solution preparation process was performed in a dry environment with dehumidifier. The water, sodium chloride and magnesium chloride hexahydrate were weighed in order. In addition, once the solution

Table 1
Experimental materials used in this work.

Chemical	Purity	Supplier
Sodium chloride (CAS:7647-14-5)	0.995 (Mass fraction)	Guangzhou chemical reagent factory
Magnesium chloride (CAS:7791-18-6)	0.99 (Mass fraction)	Eastman Kodak Laboratory Chemicals of Belgium
Carbon dioxide	0.9999 (Volume fraction)	Fushan Kede Gas Co., Ltd.
Deionized water		Laboratory-made

Table 2
Compositions of the electrolytes aqueous solutions.[a]

Code name	Composition z, mass fraction on wet basis solution	
Na2Mg8	NaCl 0.020	MgCl$_2$ 0.079
Na8Mg2	NaCl 0.080	MgCl$_2$ 0.020
Na5Mg15	NaCl 0.050	MgCl$_2$ 0.151
Na15Mg5	NaCl 0.150	MgCl$_2$ 0.050

[a] Uncertainties u is $u(z) = 0.001$.

was ready, we immediately put the electrolytes aqueous solution into the cell to start the experiment. All the chemicals were weighed on a Shanghai Jingke electronic analytical balance with a reading uncertainty of ±0.1 mg. The compositions of the electrolytes aqueous solutions were given in table 2. The magnesium chloride used in present study was magnesium chloride hexahydrate. The concentration data in table 2 were calculated considering the crystal water.

3.2. Experimental apparatus

Schematic of the experimental apparatus was shown in figure 1. The phase equilibrium condition of carbon dioxide hydrate was measured with the isochoric pressure search method [35, 36]. The stainless steel cell has a fixed volume of about 25 cm³. It can resist pressure as high as 20 MPa. A magnetic stirrer was used to facilitate the formation and decomposition of carbon dioxide hydrate. A platinum resistance thermometer (PT 100) with an uncertainty of ±0.1 K was inserted into the reactor to measure the system temperature. The pressure was detected with a pressure sensor (CYB-20S) ranged to (0−20) MPa with an uncertainty of ±0.02 MPa. The cell was put into a high and low temperature test chamber to control the temperature. The pressure and temperature of the cell were displayed and stored on a personal computer through an Agilent data acquisition.

3.3. Experimental method

Before the experiment began, the cell was thoroughly washed with deionized water, and adequately dried with air oven. Approximate 10 cm³ of the electrolytes aqueous solution was initially introduced into the cell. Air in the intake system and the cell was flushed out by carbon dioxide. The cell was pressurized up to the desired pressure by supplying carbon dioxide immediately. The isochoric pressure search method was used to find the phase equilibrium point. In this way, a pressure-temperature diagram was obtained for each experimental run, from which the hydrate dissociation point was determined. After the sample had been charged into the cell, the temperature was lowered to form hydrates. Abrupt pressure drop and temperature increase were the sign of hydrate formation. After the hydrate formed, the system temperature should be gradually increased at about 0.1 K and keep the
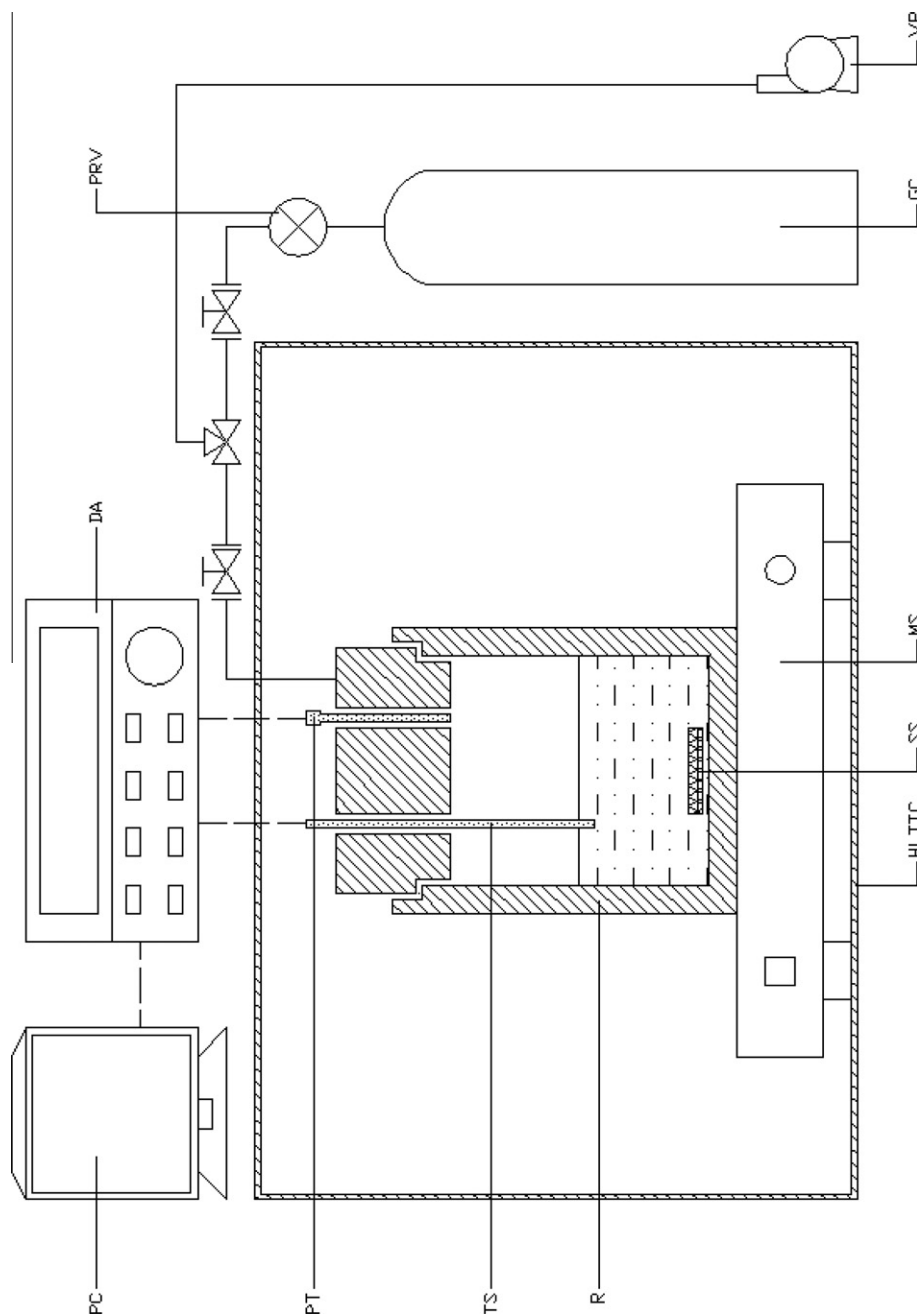
Fig. 1. Schematic diagram of experimental apparatus. PC, personal computer; DA, data acquisition; PRV, pressure regulating valve; PT, pressure transmitter; TS, temperature sensor; R, reactor; HLTTC, high and low temperature test chamber; SS, stirring seed; MS, magnetic stirrer; GC, gas cylinder; VP, vacuum pump.

temperature constant for about 4 h to achieve a steady equilibrium state at each temperature. The temperature and pressure were measured continuously. The P–T plot for hydrate formation and decomposition was observed to determine the hydrate equilibrium point. The point at which the slope of the P–T curve sharply changed was considered as the hydrate dissociation point. All the hydrate have dissociated at this point. In this way, the hydrate dissociation point was determined for one experimental run, from which the hydrate dissociation point was determined.
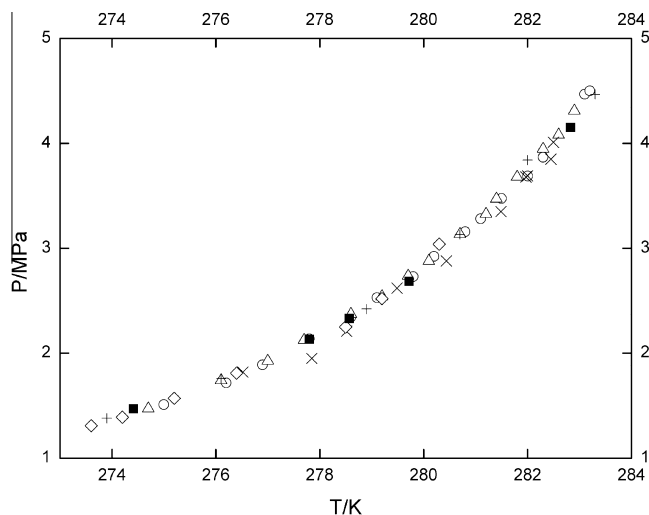
4. Results and discussion

To check the reliabilities of the experimental apparatus and experimental procedure adapted in this work, the phase equilib-

rium conditions of carbon dioxide hydrate in pure water were measured. The experimental data were listed in table 3 and plotted in figure 2 together with previous data [15–19]. Deviations of the experimental data in present study and literature [25,37,38] from the empirical correlation determined by fitting the experimental data sourced from this work with a third-order polynomial were plotted in figure 3. The deviation was defined as 100(Pexp − Pcal)/Pcal. Pexp was the experimental equilibrium pressure and Pcal was the pressure calculated by the empirical third-order polynomial correlation mentioned above. The uncertainty of the measurements in the present study was also shown in figure 3. As seen from figure 3, the deviation of the data obtained in the present study was within the uncertainty of the measurements. And the absolute average deviation was 1.84% between the data obtained in present study

TABLE 3
Phase equilibrium conditions of carbon dioxide in pure water.[a]

Phase	T/K	P/MPa
Lw-H-V	274.42	1.47
	277.80	2.13
	278.57	2.33
	279.73	2.68
	282.83	4.15

[a] Uncertainties u are $u(T)$ = 0.1 K, $u(p)$ = 0.02 MPa.

TABLE 4
Three phase equilibrium (aqueous solution + vapor + hydrate) conditions of CO_2 hydrate in electrolytes aqueous solutions.[a]

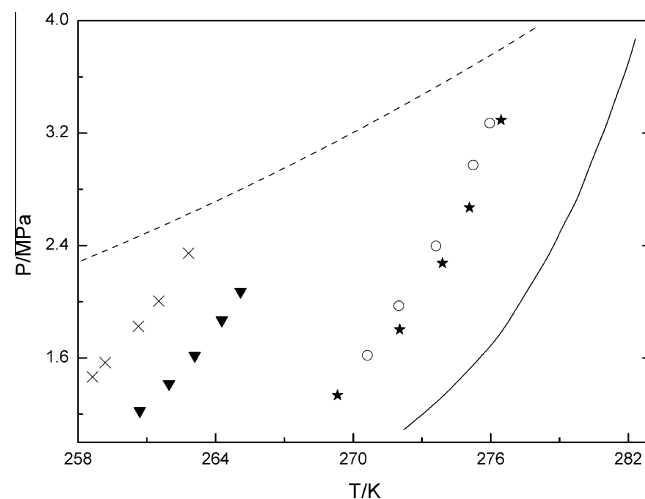| Solutions	T/K	P/MPa	Solutions	T/K	P/MPa
Na2Mg8	270.62	1.62	Na8Mg2	269.32	1.34
	271.99	1.97		272.03	1.80
	273.61	2.40		273.90	2.27
	275.23	2.97		275.07	2.67
	275.96	3.27		276.45	3.29
Na5Mg15	258.63	1.47	Na15Mg5	265.01	2.07
	259.19	1.57		264.27	1.87
	260.63	1.82		263.09	1.62
	261.53	2.00		261.97	1.42
	262.82	2.35		260.69	1.22

[a] Uncertainties u are $u(T)$ = 0.1 K, $u(p)$ = 0.02 MPa.

Fig. 2. Three phase equilibrium (aqueous solution + vapor + hydrate) conditions of carbon dioxide hydrate in pure water. ■, This work; ○, reference [18]; △, reference [19]; ×, reference [17]; +, reference [15]; ◇, reference [16].
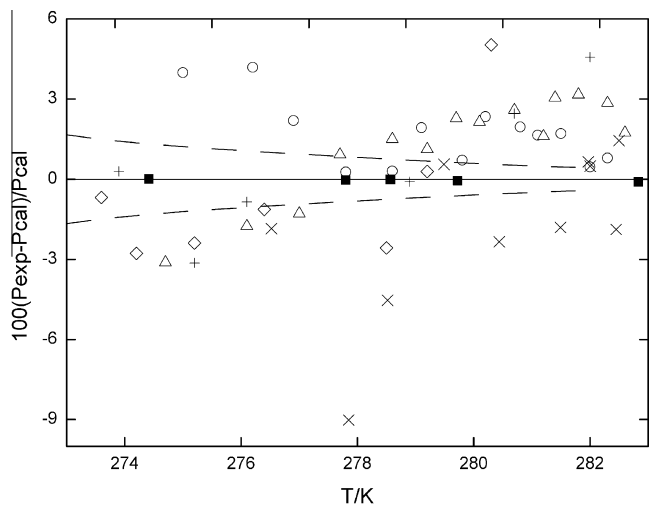
Fig. 3. Pressure deviations of the experimental data from the calculative value at a given temperature for carbon dioxide hydrate in pure water. ■, This work; ○, reference [18]; △, reference [19]; ×, reference [17]; +, reference [15]; ◇, reference [16].

Fig. 4. Three phase equilibrium (aqueous solution + vapor + hydrate) conditions of carbon dioxide hydrate in NaCl–MgCl$_2$ aqueous solutions. ○, Na2Mg8; ★, Na8Mg2; ×, Na5Mg15; ▼, Na15Mg5; —, pure water. ---, saturated vapor pressure of carbon dioxide.
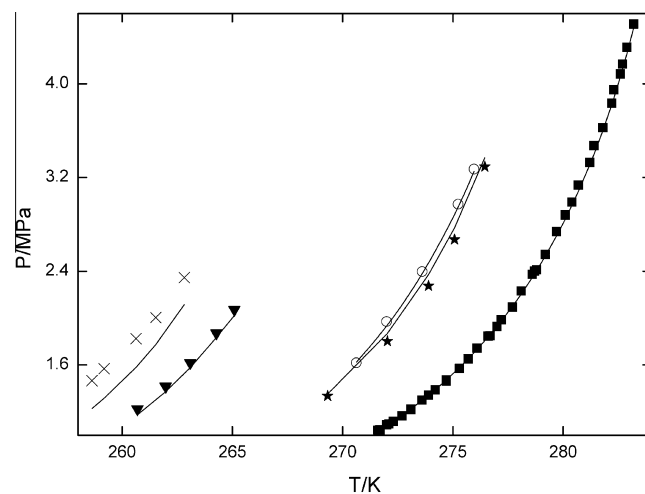
Fig. 5. Prediction of phase equilibrium (aqueous solution + vapor + hydrate) conditions of carbon dioxide hydrate in NaCl–MgCl$_2$ aqueous solutions. ■, Pure water; ○, Na2Mg8; ★, Na8Mg2; ▼, Na15Mg5; ×, Na5Mg15; —, prediction results.

and literature [15–19] with the data calculated. Difference may be caused by different measuring methods or experimental apparatus.

Experimental three phase equilibrium data of NaCl–MgCl$_2$ aqueous solutions, carbon dioxide hydrate and vapor were tabulated in table 4 and plotted in figure 4. The dotted line was the saturated vapor pressure curve of carbon dioxide [39]. Carbon dioxide

was in vapor phase area below the dotted line. The spot was the experimental data and the solid line showed the phase equilibrium conditions of carbon dioxide hydrate in pure water. The phase

equilibrium data of carbon dioxide hydrate in pure water were included to illustrate the inhibition effect of NaCl–MgCl₂. It was clearly seen that NaCl–MgCl₂ inhibited the formation of the carbon dioxide hydrate. The formation conditions of carbon dioxide hydrate in NaCl–MgCl₂ aqueous solutions were shifted to lower temperatures or higher pressures in comparison with the conditions in pure water. Figure 4 showed that the inhibition effect of Na2Mg8 was a little bit stronger than that of Na8Mg2. While the phase equilibrium conditions of carbon dioxide hydrate in Na5Mg15 aqueous solution were much more demanding than that in Na15Mg5 aqueous solution. It implied that MgCl₂ had the different inhibition effect from that of NaCl in mixed electrolytes aqueous solutions.

The prediction results of carbon dioxide hydrate phase equilibrium conditions in NaCl–MgCl₂ aqueous solutions at four experimental concentrations using the thermodynamic model were presented in figure 5. The average pressure deviation was 5.13% for four experimental concentrations, and the average deviations for (Na2Mg8, Na8Mg2, Na5Mg15, Na15Mg5) aqueous solutions were (1.294%, 3.067%, 13.384%, 2.775%), respectively. The maximum pressure deviations for (Na2Mg8, Na8Mg2, Na5Mg15, Na15Mg5) aqueous solutions were (2.624%, 4.208%, 16.211%, 2.453%), respectively. In general, the prediction results obtained from the model used in this work were in good agreement with the experimental data. The deviation for CO_2 hydrate in Na5Mg15 aqueous solutions was acceptable but not good enough. It demonstrated that the prediction accuracy for CO_2 hydrate in NaCl–MgCl₂ aqueous solutions was affected by the MgCl₂ content.

5. Conclusions

This work reported the experimental and predicted three phase equilibrium data of carbon dioxide hydrate in pure water and binary NaCl–MgCl₂ aqueous solutions at four different concentrations in temperature range of (258.63 to 276.45) K and in the pressure range of (1.34 to 3.41) MPa, respectively. The measurements were carried out by employing isochoric pressure search method with uncertainties of ±0.1 K for temperature and ±0.02 MPa for pressure. NaCl–MgCl₂ aqueous solutions inhibited carbon dioxide formation. The average pressure deviation was 5.13% and the prediction accuracy obtained from the used model was acceptable.

Acknowledgements

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