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Experimental and modeling studies on the hydrate formation of CO_2 and CO_2-rich gas mixtures

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Abstract

The hydrate formation conditions of CO_2 and CO_2-rich gas mixtures (CO_2>90 mol%) containing $N_2/CH_4/C_2H_6$ and ($N_2+CH_4+C_2H_6$) in the presence of aqueous solutions of ethylene glycol were measured in a sapphire cell equipped with magnetic stirrer and data acquisition system. Isothermal pressure-search method was adapted in the pressure range of 0.8–3.5 MPa and a temperature range of 267.2–279.7 K. Eight systems have been studied and a total of 36 data points were measured.

In the modeling part, the hydrate models recently developed by this group (Chen–Guo and Zuo–Guo model) and a typical literature reported van der Waals–Platteeuw type model were tested against the hydrate formation data of CO_2-rich gas mixtures in water and aqueous solutions of ethylene/sodium chloride. The performance of various models is evaluated.

Keywords: CO_2-rich gas mixtures; Hydrate formation; Data; Model; Ethylene glycol

1. Introduction

Carbon dioxide plays important role in the enhanced oil recovery (EOR) process. The large amount of carbon dioxide required is usually provided by CO_2-reservoirs in situ, however, the gas sources are not pure CO_2, significant amounts of CH_4, C_2H_6 and N_2 are generally present. As the hydrate formation temperature is rather high (compared to methane), there is a risk of hydrate formation during its production and transportation which could cause blocking of the pipeline/equipment.

On the other hand, hydrates of CO_2/CO_2-rich gas mixtures are of significance in the environmental protection aspect. For depressing the global warming process, it has been suggested to convert the CO_2 in the industrial flue gases into hydrate form [1]. Since the specific gravity of CO_2-hydrate is greater than seawater, it can be sunk to the deep ocean.

In addition, new technologies based on CO_2/CO_2-rich gas hydrates could be developed, such as the transportation/storage of CO_2/CO_2-rich gases in solid form.

In a recent paper [2], we have reviewed the previous experimental studies on the hydrate formation of CO_2 and CO_2-containing gas mixtures, and reported the hydrate formation data of CO_2 and CO_2-rich (CO_2>90 mol%) gas mixtures in water and aqueous solutions of sodium chloride.

The major objectives of this work are:

1. Measure the hydrate formation data of CO_2 and CO_2-rich gas mixtures in aqueous solutions of ethylene glycol (EG), to supplement the data recently measured in aqueous solutions of sodium chloride [2].
2. Examine the performance of three hydrate models: i.e. the Chen–Guo model [3] and Zuo–Guo model [4] developed by this laboratory and the van der Waals–Platteeuw type model adapted in the CSMHYD program [5] on the studied systems.

2. Experimental

2.1. Apparatus

The apparatus used in this work is the same as that reported in the previous papers [2,6,7]. The schematic diagram of the apparatus is shown in Fig. 1. The apparatus consists of a cylindrical transparent sapphire cell (2.5 cm i.d., effective volume 60 cm^3) installed in an air bath, a magnetic stirrer is equipped for accelerating the equilibrium process. The formation/dissociation of hydrate crystals in the solution can be observed directly through the transparent sapphire cell. The accuracy of temperature and pressure measurements is

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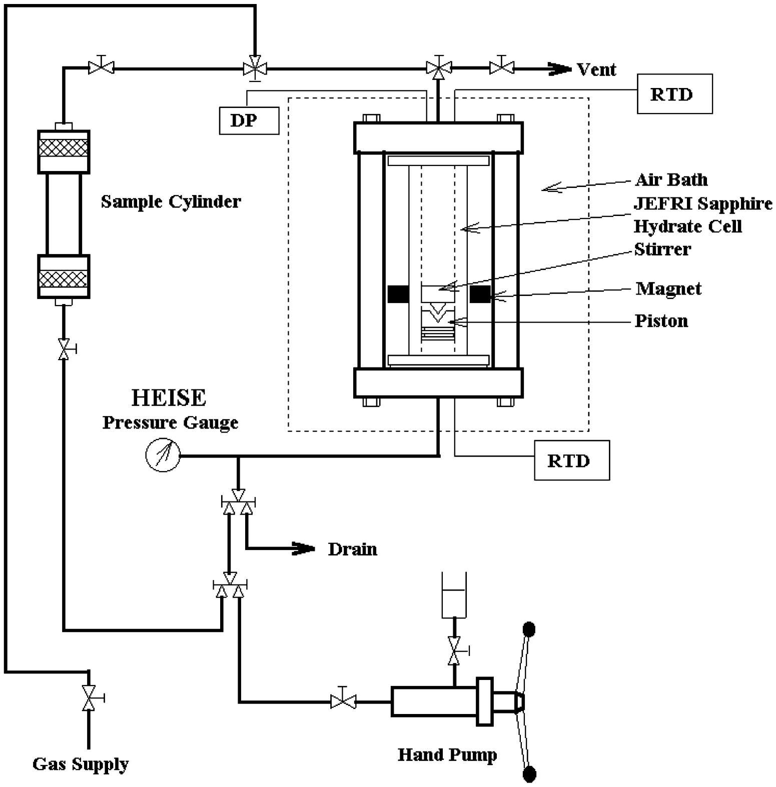

Fig. 1. Schematic diagram of the experimental system. DP: differential transducer, RTD: resistance thermocouple detector.

±0.2 K and ±0.025 MPa, respectively. The detailed description of the apparatus is referred to [2,6,7].

2.2. Materials and preparation of samples

Research grade (99.99%) carbon dioxide, methane, ethane and nitrogen purchased from AP Beifen Gas Industry Corporation were used in preparing the test samples. The compositions of the three binary gas mixtures (CO_2+CH_4), (CO_2+C_2H_6), (CO_2+N_2) and a quaternary gas mixture (CO_2+CH_4+C_2H_6+N_2) were analyzed using gas chromatography (H-P 5890A).

Research grade ethylene glycol (EG) were used for preparing the aqueous EG solutions, which were supplied by the Beijing Reagents Corporation. The deionized water was re-distilled in this laboratory prior using. Appropriate amount of EG and deionized water was weighed on an electronic balance, which has a precision of ±0.1 mg, and then mixed thoroughly at room temperature.

2.3. Experimental procedure

The experimental procedure adapted in this work is exactly the same with what we described in [2].

2.4. Experimental results

The eight CO_2/CO_2-rich systems studied are tabulated in Table 1. The measured hydrate formation data for pure CO_2 in water and 10 mass% methanol/EG solutions are given in Table 2. The similar data measured for binary and quaternary CO_2-rich gas mixtures in aqueous solutions of EG are listed in Tables 3 and 4, respectively.

Table 1
Systems studied in this work

System No.	Gas phase (mol%)	Aqueous phase (mass%)
1	CO_2	Water
2	CO_2	10.00% Methanol
3	CO_2	10.04% EG
4	96.52% CO_2+3.48% CH_4	10.00% EG
5	94.69% CO_2+5.31% C_2H_6	10.06% EG
6	90.99% CO_2+9.01% N_2	13.01% EG
7	96.52% CO_2+3.48% N_2	10.00% EG
8	88.53% CO_2+6.83% CH_4+ 0.38% C_2H_6+4.26% N_2	10.00% EG

Table 2
Measured hydrate formation data for carbon dioxide in water and aqueous solutions of methanol and ethylene glycol

Aqueous phase	Temperature (K)	Pressure (MPa)
Water	274.7	1.50
	277.5	2.03
	279.7	2.78
10.0 mass% methanol	271.6	1.74
	273.8	2.35
10.04 mass% EG	270.9	1.15
	273.1	1.74
	275.8	2.40
	278.3	3.20

Table 3
Measured hydrate formation data of CO_2-rich binary gas mixtures in the presence of aqueous EG solutions

Binary gas mixture (mol%)	Aqueous phase (mass%)	Temperature (K)	Pressure (MPa)
96.52% CO_2+3.48% CH_4	10.00 EG	268.7	1.14
		271.3	1.60
		274.2	2.26
		278.0	3.22
94.69% CO_2+5.31% C_2H_6	10.60 EG	269.1	0.85
		271.0	1.03
		272.9	1.31
		274.9	1.82
		276.4	2.31
96.52% CO_2+3.48% N_2	10.00 EG	268.9	1.00
		272.1	1.35
		273.4	1.62
		276.1	2.49
90.99% CO_2+9.01% N_2	13.01% EG	267.2	0.93
		267.9	1.03
		270.2	1.20
		271.9	1.76
		273.7	2.15
		274.2	2.49
		275.3	2.80
		276.5	3.39

For checking the experimental apparatus and procedure adapted in this work, the hydrate formation pressures of pure carbon dioxide in water and 10 mass% methanol solution were measured (data listed in Table 2). The comparison of the measured data for CO_2-water system with literature data [8–10] is shown in Fig. 2. It can be seen from Fig. 2 that our data for pure CO_2 in water match the literature data very well. However, for CO_2 hydrate formation in 10 mass% methanol solution, inconsistencies were observed between the data measured by Dholabhai et al. [9] and Ng and Robinson [10]. Our data are in close agreement with those reported by Dholabhai et al. [9], however, deviate somewhat from the data measured by Ng and Robinson [10]. The hydrate formation data for pure CO_2 in 10 mass% EG solution (not previously reported) are also given in Table 2. It is shown that the inhibition effect of EG is inferior to that of methanol.

The hydrate formation data of the three above mentioned CO_2-rich gas binaries in aqueous solutions of EG (listed in Table 3) are plotted in Figs. 3–5. For comparing the inhibition effects, the hydrate formation data of the corresponding binary gas mixtures in water and in NaCl solution [2] are also included.

Table 4
Measured hydrate formation data of a CO_2-rich quaternary gas mixture containing (mol%) 88.53% CO_2, 6.83% CH_4, 0.38% C_2H_6, and 4.26% N_2 in the presence of aqueous EG solutions

Aqueous phase	Temperature (K)	Pressure (MPa)
10.0 mass% EG solution	268.8	0.80
	270.7	1.16
	274.4	1.82
	276.4	2.41
	278.1	2.85
	279.3	3.50

3. Modeling

3.1. Hydrate models tested

Three hydrate models were used to predict the hydrate formation data measured for pure CO_2 and CO_2-rich gas mixtures in water and aqueous solutions of EG and NaCl:

- Chen–Guo model [3].
- Zuo–Guo model [4].

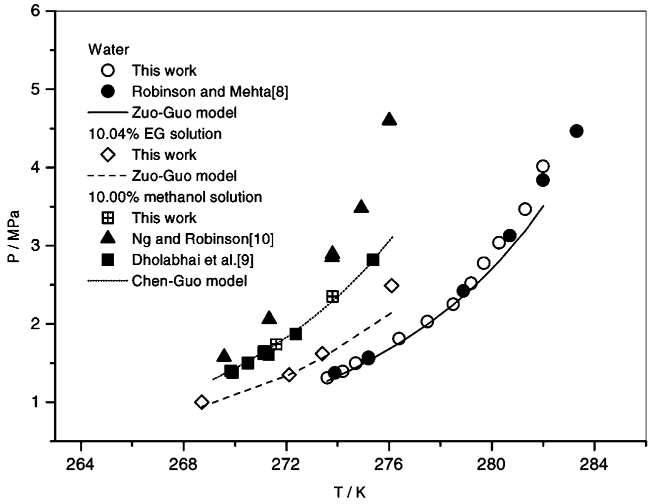

Fig. 2. Comparison of the hydrate formation data for carbon dioxide in water, in 10.04 mass% EG solution and in 10 mass% methanol solutions measured by the authors and reported in literature.

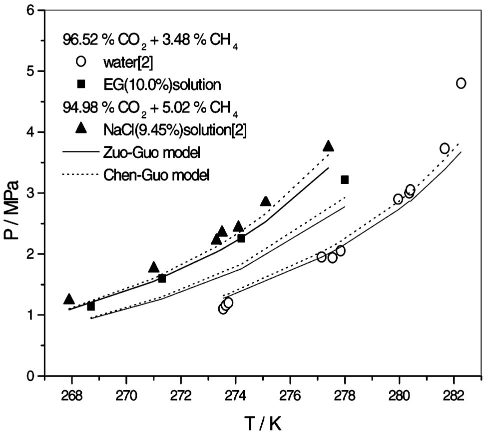

Fig. 3. Comparison of Chen–Guo model and Zuo–Guo model in predicting the hydrate formation of a methane containing CO_2-rich binary gas mixture in water and in aqueous EG/NaCl solutions.

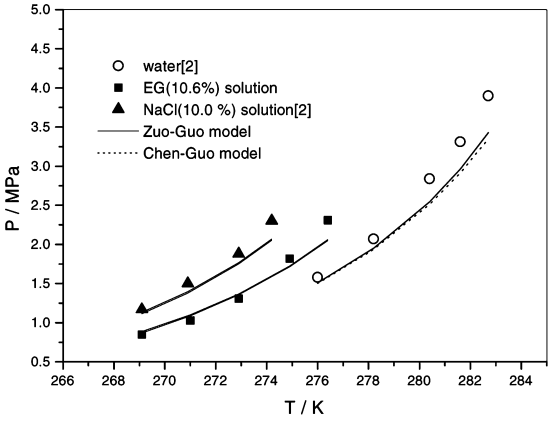

Fig. 4. Comparison of Chen–Guo model and Zuo–Guo model in predicting the hydrate formation of an ethane containing CO_2-rich binary gas mixture in water and in aqueous EG/NaCl solutions.

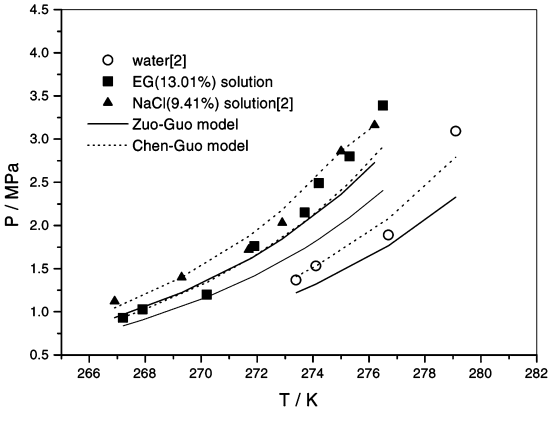

Fig. 5. Comparison of Chen–Guo model and Zuo–Guo model in predicting the hydrate formation of a nitrogen containing CO_2-rich binary gas mixture in water and in aqueous EG/NaCl solutions.

- The van der Waals–Platteeuw (vdW–P) type model adapted in the CSMHYD hydrate program [5].

The Chen–Guo model [3] developed, based on a new approach, was originally for applying to gas–water systems. In this work, it has been extended to systems containing electrolyte/polar inhibitor in the aqueous phase by applying the modified Patel and Teja equation of state (MPT EOS) proposed by Zuo and Guo [11] to calculate the activity of water in the aqueous phase.

The Zuo–Guo model developed in 1996 [4] is a generalized hydrate model applicable to electrolyte/polar inhibitor containing systems, which is based on a simplified multi-shell vdW–P type model and the MPT EOS.

The vdW–P type model used in the original CSMHYD hydrate program [5] is restricted to gas–water systems.

The detailed mathematical descriptions of the three tested hydrate models are referred to the original articles.

3.2. Prediction results and discussion

The absolute average deviations of predicted temperature (AADT, %) and pressure (AADP, %) are defined as follows:

$$\mathrm{AADP}(\%) = \left(\frac{1}{N_\mathrm{p}}\right)\sum_{j=1}^{N_\mathrm{p}}\left[\frac{T_\mathrm{cal}-T_\mathrm{exp}}{T_\mathrm{exp}}\right]_j \times 100 \qquad (1)$$

$$\mathrm{AADP}(\%) = \left(\frac{1}{N_\mathrm{p}}\right)\sum_{j=1}^{N_\mathrm{p}}\left[\frac{P_\mathrm{cal}-P_\mathrm{exp}}{P_\mathrm{exp}}\right]_j \times 100 \qquad (2)$$

where N_p denotes the number of data points.

The prediction results of the hydrate formation conditions of CO_2/CO_2-rich gas mixtures in water and in aqueous solutions of ethylene glycol/sodium chloride are tabulated in Tables 5–7 and plotted in Figs. 3–6. *It should be emphasized that no adjustable parameter was involved in the calculations.*

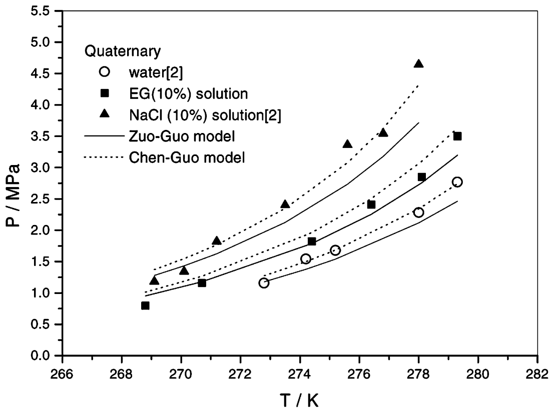

Fig. 6. Comparison of Chen–Guo model and Zuo–Guo model in predicting the hydrate formation of a CO_2-rich quaternary gas mixture containing (mol%) 88.53% CO_2, 6.83% CH_4, 0.38%C_2H_6, and 4.26% N_2 in water and in aqueous EG/NaCl solutions.

Table 5
Prediction results of the hydrate formation conditions of CO_2/CO_2-rich gas mixtures in water (experimental data are taken from [2] if not otherwise specified)

System[a]	*T*-range (K)	*P*-range (MPa)	N_p	AADT (%)			AADP (%)		
				Chen–Guo	Zuo–Guo	CSMHYD	Chen–Guo	Zuo–Guo	CSMHYD
CO_2[b]	273.9–282.0	1.38–3.84	6	0.0478	0.1330	0.0465	1.7987	4.5260	1.7466
CO_2	273.6–282.0	1.31–4.02	12	0.0709	0.1329	0.0887	2.5074	4.5344	3.1858
4	273.5–282.3	1.10–4.02	11	0.2493	0.2472	0.7724	8.7730	8.4881	11.0155
5	276.0–282.7	1.58–3.90	5	0.2505	0.2168	0.2216	8.5658	7.6183	7.6850
6	273.1–280.2	1.22–2.95	5	0.0926	0.2758	NC[c]	3.1354	8.6746	NC
7	273.4–279.1	1.37–3.09	4	0.1667	0.4808	NC	5.6335	13.9401	NC
8	272.8–279.3	1.16–2.77	5	0.1006	0.2535	NC	3.3130	7.6758	NC

[a] Compositions of mixtures are given in Table 1.
[b] Data from Sloan [5].
[c] NC: not converged.

Table 6
Prediction results of the hydrate formation conditions of CO_2/CO_2-rich gas mixtures in aqueous ethylene glycol (EG) solutions

System[a]	EG mass% in aq. phase	*T*-range (K)	*P*-range (MPa)	N_p	AADT (%)		AADP (%)	
					Chen–Guo	Zuo–Guo	Chen–Guo	Zuo–Guo
CO_2	10.04	270.9–278.3	1.15–3.20	4	0.2344	0.3146	7.7067	9.9196
4	10.0	268.7–278.0	1.14–3.22	4	0.5439	0.6619	16.2733	19.0025
5	10.6	269.1–276.4	0.85–2.31	5	0.1711	0.1926	5.5099	6.1357
6	13.01	267.2–276.5	0.93–3.39	8	0.2525	0.6686	8.3399	18.7619
7	10.0	268.9–276.1	1.00–2.49	4	0.1359	0.2077	4.5630	6.3013
8	10.0	268.8–279.3	0.80–3.59	6	0.2714	0.2126	9.6182	6.9112

[a] Compositions of mixtures are given in Table 1.

Table 7
Prediction results of the hydrate formation conditions of CO_2-rich gas mixtures in aqueous sodium chloride solutions (experimental data are taken from [2])

System[a]	NaCl mass% in aq. phase	*T*-range (K)	*P*-range (MPa)	N_p	AADT (%)		AADP (%)	
					Chen–Guo	Zuo–Guo	Chen–Guo	Zuo–Guo
4	9.45	267.9–277.4	1.24–3.75	7	0.1926	0.3227	6.3416	10.1610
5	10.60	269.1–274.2	1.17–2.30	4	0.2125	0.1850	6.8736	5.8824
6	9.41	266.9–276.2	1.12–3.16	7	0.1576	0.4021	5.4963	11.9136
8	10.00	269.1–278.0	1.18–4.64	7	0.2122	0.3779	7.6317	12.2113

[a] Compositions of mixtures are given in Table 1.

From Table 5, it can be seen that Chen–Guo model gives the best predictions for the CO_2-rich gas mixture–water systems. The CSMHYD program failed to converge for certain systems. Tables 6 and 7 again show that, in general, Chen–Guo model gives better predictions for the systems containing EG/NaCl, as compared to Zuo–Guo model [4].

4. Conclusions

In this work, the hydrate formation data of CO_2 and CO_2-rich gas mixtures in aqueous ethylene glycol solutions had been measured, which are supplementary to our previous data measured in aqueous NaCl solutions. The measured data are useful for evaluating the performance of the existing hydrate models on such industrially significant systems.

By introducing the MPT EOS [11] to evaluate the activity of water in aqueous phase, the Chen–Guo hydrate model [3] has been successfully extended to systems containing salt and polar inhibitors. In general, better results were observed as compared to Zuo–Guo model [4].

Acknowledgements

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