Hydrate Formation of CO_2-Rich Binary and Quaternary Gas Mixtures in Aqueous Sodium Chloride Solutions

Shuan-Shi Fan† **and Tian-Min Guo***

High Pressure Fluid Phase Behavior & Property Research Laboratory, University of Petroleum, P.O. Box 902, Beijing 100083, People's Republic of China

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Hydrate formation data of CO_2-rich mixtures, three binaries (CO_2 + CH_4, CO_2 + C_2H_6 and CO_2 + N_2) and one quaternary (CO_2 + CH_4 + C_2H_6 + N_2), in water and aqueous sodium chloride solutions were measured. The measurements were carried out in a transparent sapphire cell by applying an isothermal pressure search method in the temperature range 264 K to 284 K and the pressure range 0.5 MPa to 5.0 MPa.

Introduction

Carbon dioxide plays an important role in the enhanced oil recovery process. The huge amount of carbon dioxide required is usually provided by a CO_2 reservoir in situ; however, the gas stored in the reservoir is not pure CO_2. Some minor components such as CH_4, C_2H_6, and N_2 are present. Since the hydrate formation temperature of CO_2-rich gas is rather high (compared to methane), there is a greater risk of hydrate formation during its production and transportation, which could cause blocking of the pipeline or equipment.

On the other hand, the transportation and storage of CO_2 or CO_2-rich gas in solid (hydrate) form could be realized, as has been thoroughly studied in Norway for natural gas mixtures (Gudmundsson and Borrehaug, 1996).

Carbon dioxide-rich gas hydrates are of significance for environmental protection aspects also. For depressing the global warming process, it has been suggested to convert CO_2 in industrial flue gas into hydrate form (Saji et al., 1992). Since the specific gravity of CO_2-hydrate is larger than that sea of water, it can be sunk deep in the ocean.

Numerous hydrate formation data for pure carbon dioxide and its binary mixtures in the presence of water have been reported in the literature. However, only a few binary systems containing a high concentration of CO_2 have been studied. Unruh and Katz (1949) reported the hydrate formation data for a (CO_2 + CH_4) system with a maximum CO_2 concentration of 60 mol %. Berecz and Balla-Achs (1983) also measured the data for the same binary system. Adisasmito et al. (1991) confirmed and extended the data reported by Unruh and Katz (1949). Robinson and Mehta (1971) measured the data for a (CO_2 + C_3H_8) system in the CO_2 concentration range 16.0 mol % to 94.5 mol %. Adisasmito and Sloan (1992) reported the hydrate formation conditions of hydrocarbon gases containing appreciable amounts of carbon dioxide.

For inhibitor-containing systems, Bishnoi's group at the University of Calgary systematically studied the hydrate formation of CO_2 in aqueous solutions of electrolytes/methanol (Dholabhai et al., 1991, 1993, 1996, 1997; Bishnoi and Dholabhai, 1993; Parent, 1993; Dholabhai and Bishnoi, 1994). Tohidi et al. (1997) measured the data for the hydrate-free zone of a number of pure gases (including CO_2) and multicomponent reservoir fluids in the presence of single/mixed electrolyte solutions. However, hydrate formation data of CO_2-rich (>90 mol %) gas mixtures containing small amounts of minor components (CH_4, C_2H_6, and N_2) in water and in brine are very scarce in the literature.

In this work, hydrate formation data in the presence of water and aqueous sodium chloride solutions (~10 mass %) for three CO_2-rich binary gas mixtures (CO_2 + CH_4, CO_2 + C_2H_6, and CO_2 + N_2) and a quaternary gas mixture (CO_2 + CH_4 + C_2H_6 + N_2) have been measured.

Experimental Section

Apparatus. The apparatus used in this work is the same as that reported in our previous work (Mei et al., 1996, 1998). The schematic diagram of the apparatus is given in Figure 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 with a magnetic stirrer for accelerating the equilibrium process. The formation/dissociation of hydrate crystals in the solution can be observed directly through the transparent sapphire cell. The accuracies of temperature and pressure measurements are ±0.2 K and ±0.025 MPa, respectively. A detailed description of the apparatus is given by Mei et al. (1996, 1998).

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 gas mixtures were analyzed using gas chromatography (Hewlett-Packard Corp., Model 5890A).

Research grade sodium chloride was used for preparing the aqueous solutions and was supplied by the Beijing Reagents Corporation. The deionized water was redistilled prior to use. Appropriate amounts of NaCl and deionized water were weighed on an electronic balance, which has a precision of ±0.1 mg, and then mixed thoroughly at room temperature. For ensuring no salt precipitation occurred, the flasks containing the prepared brines were inserted into the air bath maintained at the lowest experimental temperature for 24 h.

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* Corresponding author. Telephone: 86-10-62340132. Fax: 86-10-62340132. E-mail: guotm@public.iuol.net.cn.

† Current address: Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510070, People's Republic of China. E-mail: fanss@ms.giec.ac.cn.

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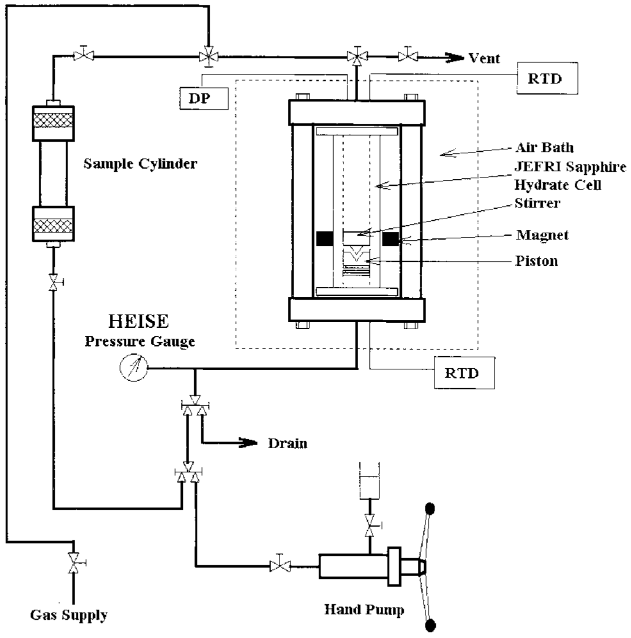

Figure 1. Schematic flow diagram of the experimental system: DP, differential transducer; RTD, resistance thermocouple detector.

Experimental Procedure. Prior to charging it with a solution, the cell was rinsed with deionized water to wash out the residual solution remaining from the previous experiment. The cell was then rinsed once again with the experimental solution. About 15 cm^3 of feed liquid (water/aqueous sodium chloride solution) was added to the thoroughly cleaned sapphire cell. The cell was then repeatedly flushed with the feed gas. A sample from the vapor phase of the cell was analyzed to ensure the absence of air. Then the system was maintained at the selected temperature.

For eliminating the hysteresis effect in hydrate formation, the hydrate crystals were first formed by raising the system pressure via the floating piston to ~2.0 MPa above the estimated hydrate formation pressure (using in-house software). The hydrates formed were decomposed slowly by gradually lowering the system pressure. This was accomplished by increasing the volume of the cell by moving the piston downward. Once the hydrates were decomposed, the system pressure was raised to form the hydrates again. In each run, the above process was repeated for two to three times.

The system pressure was then adjusted to the expected equilibrium value and left to equilibrate. If the temperature and pressure of the system remained constant for 4−6 h with a trace amount of hydrate crystal present (usually cling to the wall of the sapphire cell), the system temperature and pressure were taken as the equilibrium value and recorded. If all the hydrates were decomposed (no hydrate shown up), then the hydrates were formed once again by adjusting the system pressure to a slightly higher value (at a pressure step ~ 0.05 MPa) and the observation was repeated. On the other hand, if the pressure is higher than the equilibrium value, it should be reduced at the same pressure step, and the inspection should be repeated. Once the equilibrium conditions were established, the system pressure was reduced by about 0.05 MPa to verify that all the hydrates were decomposed, and then the experiment was terminated. The above procedure was repeated for a series of selected temperatures.

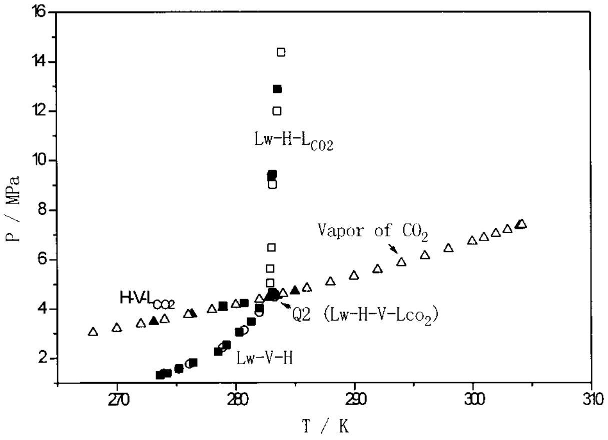

Figure 2. Measured hydrate formation data of pure carbon dioxide in water and comparison with literature data: (▲) Larson (1955); (□) Ng and Robinson (1985); (○) Robinson and Mehta (1971); (■) this work; (△) vapor of CO_2 from Angus (1976).

Table 1. Measured Hydrate Formation Conditions for Pure CO_2 in Water

phase	T/K	P/MPa
L_W-H-V	273.6	1.31
	274.2	1.39
	275.2	1.57
	276.4	1.81
	278.5	2.25
	279.2	2.52
	280.3	3.04
	281.3	3.47
	282.0	4.02
$L_{CO_2}-H-V$	278.9	4.12
	280.7	4.23
$Q2(L_{CO_2}-H-L_W-V)$	283.1	4.65
$L_{CO_2}-H-L_W$	283.1	9.32
	283.2	9.43
	283.6	12.87

Experimental Results and Discussion

Hydrate Formation of Pure Carbon Dioxide in Water. For checking the experimental apparatus and procedure adapted in this work, the hydrate formation pressures of carbon dioxide in water were measured and compared with the data reported in the literature (Larson, 1955; Deaton and Frost, 1946; Robinson and Mehta, 1971; Ng and Robinson, 1985). The measured data are listed in Table 1, and the comparison with literature data is plotted in Figure 2. It can be seen from Figure 2 that the data measured in this work match very well with the earlier literature data. It should be emphasized that the reproducibility of the hydrate formation pressures reported in this work is good.

Hydrate Formation of CO_2-Rich Binary Gas Mixtures in Water. The compositions of the three CO_2-rich binary gas mixtures studied ($CO_2 + CH_4$, $CO_2 + C_2H_6$, and $CO_2 + N_2$) and the measured hydrate formation data in water are presented in Table 2. The contents of the minor components in the CO_2-rich gas mixtures are close to those found in the CO_2 reservoirs discovered in China.

The hydrate formation pressure of the binary mixture containing 3.48 mol % CH_4 is slightly higher than that of pure carbon dioxide. The presence of nitrogen leads to a significant increase of hydrate formation pressure, and it is quite sensitive to the nitrogen content (9.01 mol % compared with 3.48 mol %). On the other hand, the presence of 5.31 mol % ethane in the CO_2-rich binary leads to a small decrease of hydrate formation pressure. Adisasmito and Sloan (1992) have studied the hydrate forma-

Table 2. Hydrate Formation Conditions of CO_2-Rich Binary Gas Mixtures in the Presence of Water and Aqueous NaCl Solutions

binary gas mixture	aqueous phase	*T*/K	*P*/MPa
96.52 mol % CO_2 + 3.48 mol % CH_4	water	273.5	1.10
		273.6	1.16
		273.7	1.20
		277.2	1.95
		277.6	1.94
		277.9	2.05
		280.4	3.00
		281.7	3.73
		282.3	4.80
94.98 mol % CO_2 + 5.02 mol % CH_4	9.45 mass % NaCl	267.9	1.24
		271.0	1.76
		273.3	2.22
		273.5	2.35
		274.1	2.43
		275.1	2.85
		277.4	3.75
94.69 mol % CO_2 + 5.31 mol % C_2H_6	water	276.0	1.58
		278.2	2.07
		280.4	2.84
		281.6	3.31
		282.7	3.90
	10.0 mass % NaCl	269.1	1.17
		270.9	1.50
		272.9	1.88
		274.2	2.30
96.52 mol % CO_2 + 3.48 mol % N_2	water	273.1	1.22
		274.6	1.54
		278.3	2.42
		279.4	2.89
		280.2	2.95
90.99 mol % CO_2 + 9.01 mol % N_2	water	273.4	1.37
		274.1	1.53
		276.7	1.89
		279.1	3.09
	9.41 mass % NaCl	266.9	1.12
		269.3	1.40
		271.7	1.72
		271.8	1.74
		272.9	2.03
		275.0	2.86
		276.2	3.16

tion of a similar binary mixture (96.0 mol % CO_2 + 4.0 mol % C_2H_6), and the same effect of the presence of ethane was observed.

Hydrate Formation of CO_2-Rich Binary Gas Mixtures in Aqueous NaCl Solutions. The hydrate formation data of the above-mentioned three CO_2-rich binary gas mixtures in aqueous NaCl solutions are given in Table 2 and plotted in Figures 3–5. The hydrate formation data of the corresponding binary gas mixtures in water are included in each figure for illustrating the inhibiting effect of NaCl. The solid curves drawn in the figures are calculated using the generalized Zuo–Guo hydrate model (Zuo et al., 1996; Mei et al., 1996).

It can be seen that NaCl exhibits a significant inhibiting effect. At a given pressure, the hydrate formation temperature in aqueous solution containing 10 mass % NaCl is lower than that in water. For example, the depression of the formation temperature at a pressure of 1.82 MPa for the binary mixture containing 94.69 mol % CO_2 and 5.31 mol % C_2H_6 is 4.5 K.

The predicted results based on the Zuo–Guo model are in fair agreement with the experimental data. Further modeling work is underway.

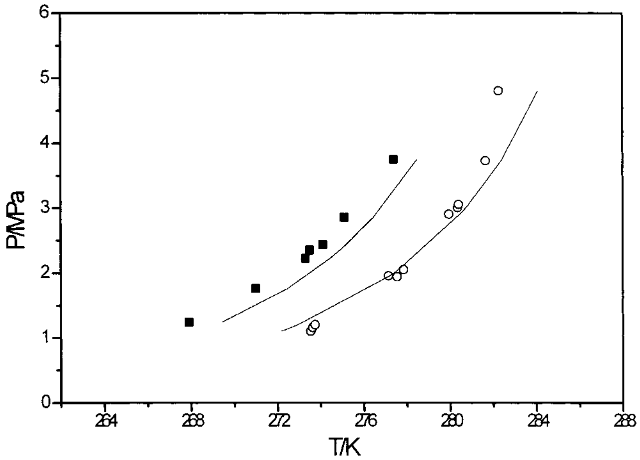

Figure 3. Hydrate formation of CO_2-rich binary mixtures: (○) containing 3.48 mol % CH_4 in water; (■) containing 5.02 mol % CH_4 in 9.45 mass % aqueous NaCl solution; (—) predicted by the Zuo–Guo model (1996).

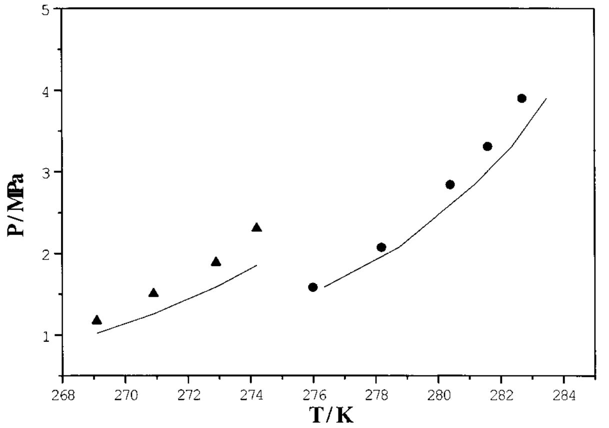

Figure 4. Hydrate formation of a CO_2-rich binary mixture containing 5.31 mol % C_2H_6 in water and in aqueous NaCl solution: (●) water; (▲) 10 mass % NaCl; (—) predicted by the Zuo–Guo model (1996).

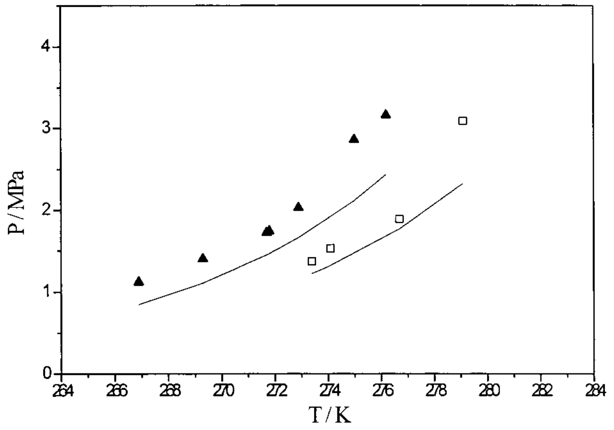

Figure 5. Hydrate formation of a CO_2-rich binary gas mixture containing 9.01 mol % N_2 in water and in aqueous NaCl solution: (□) water; (▲) 9.41 mass % NaCl; (—) predicted by the Zuo–Guo model (1996).

Hydrate Formation of a Quaternary CO_2-Rich Gas Mixture. Table 3 presents the hydrate formation data for a quaternary CO_2-rich gas mixture (sampled from a Chinese reservoir) in water and in 10.0 mass % NaCl solution. The composition (mol %) of the quaternary mixture is 88.53% CO_2, 6.83% CH_4, 0.38% C_2H_6, and 4.26% N_2. The inhibiting effect of NaCl (10.0 mass %) in the aqueous phase is distinctively shown in Figure 6. It is interesting to note that the hydrate formation pressure of this quaternary gas mixture in water is close to that of pure CO_2 in water. This is due to the cancellation of the effects

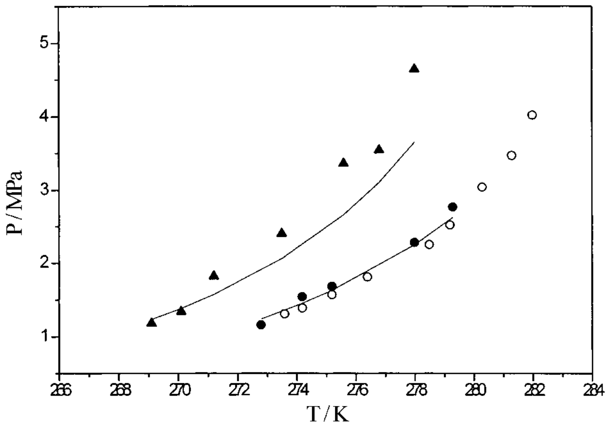

Figure 6. Hydrate formation of a CO_2-rich quaternary gas mixture containing 88.53 mol % CO_2, 6.83 mol % CH_4, 0.38 mol % C_2H_6, and 4.26% mol % N_2 in water and in aqueous NaCl solution: (●) water; (▲) 10 mass % NaCl; (○) CO_2 in water; (—) predicted by Zuo−Guo model (1996).

Table 3. Hydrate Formation Conditions of a CO_2-Rich Quaternary Gas Mixture Containing 88.53 mol % CO_2, 6.83 mol % CH_4, 0.38 mol % C_2H_6, and 4.26 mol % N_2 in the Presence of Water and Aqueous NaCl Solution

aqueous phase	*T*/K	*P*/MPa
water	272.8	1.16
	274.2	1.54
	275.2	1.68
	278.0	2.28
	279.3	2.77
10.0 mass % NaCl solution	269.1	1.18
	270.1	1.34
	271.2	1.82
	273.5	2.40
	275.6	3.36
	276.8	3.54
	278.0	4.64

of the presence of CH_4, C_2H_6, and N_2 simultaneously in the mixture.

Conclusions

In this work, the effect of the presence of methane/ethane/nitrogen in CO_2-rich gas mixtures on the hydrate formation conditions in water/aqueous NaCl solutions (containing ~10 mass % NaCl) were determined. Similar data were measured for a quaternary CO_2-rich gas mixture containing methane, ethane, and nitrogen simultaneously. The measured data are useful for testing the applicability of the existing hydrate models to CO_2-rich gas mixtures.

Literature Cited

Adisasmito, S.; Sloan, E. D., Jr. Hydrates of hydrocarbon gases containing carbon dioxide. *J. Chem. Eng. Data* **1992**, *37*, 343−349.

Adisasmito, S.; Frank, R. J.; Sloan, E. D., Jr. Hydrates of carbon dioxide and methane mixtures. *J. Chem. Eng. Data* **1991**, *36*, 68−71.

Angus, S.; Armstrong, B.; de Reuck, K. M. *International thermodynamic tables of the fluid state. Vol. 3. Carbon dioxide.* IUPAC, 1976.

Berecz, E.; Balla-Achs, M. *Studies in Inorganic Chemistry 4: Gas Hydrates*; Elsevier: Amsterdam, 1983.

Bishnoi, P. R.; Dholabhai, P. D. Experimental study on propane hydrate equilibrium conditions in aqueous electrolyte solutions. *Fluid Phase Equilib.* **1993**, *83*, 455−462.

Deaton, W. M.; Frost, E. M., Jr. *Clathrate hydrate and their relation to the operations of natural gas pipeline*; U.S. Bureau of Mines Monograph 8; U.S. Bureau of Mines: Washington, DC, 1946.

Dholabhai, P. D.; Bishnoi, P. R. Hydrate equilibrium conditions in aqueous electrolyte solutions: Mixture of methane and carbon dioxide. *J. Chem. Eng. Data* **1994**, *39*, 191−194.

Dholabhai, P. D.; Englezos, P.; Kalogerakis, N.; Bishnoi, P. R. Equilibrium conditions for hydrate formation from binary mixtures of methane and carbon dioxide in the presence of electrolytes, methanol and ethylene glycol. *Can. J. Chem. Eng.* **1991**, *69*, 800−805.

Dholabhai, P. D.; Kalogerakis, N.; Bishnoi, P. R. Equilibrium conditions for carbon dioxide hydrate formation in aqueous electrolyte solutions. *J. Chem. Eng. Data* **1993**, *38*, 650−654.

Dholabhai, P. D.; Parent J. S.; Bishnoi P. R. Carbon dioxide hydrate equilibrium conditions in aqueous solutions containing electrolytes and methanol using a new apparatus. *Ind. Eng. Chem. Res.* **1996**, *35*, 819−823.

Dholabhai, P. D.; Parent, J. S.; Bishnoi, P. R. Equilibrium conditions for hydrate formation from binary mixtures of methane and carbon dioxide in the presence of electrolytes, methanol and ethylene glycol. *Fluid Phase Equilibr.* **1997**, *141*, 235−246.

Gudmundsson, J.; Borrehaug, A. Frozen hydrate for transport of natural gas. *Proceedings of the 2nd International Conference on Natural Gas Hydrates*, June 2−6, 1996, Toulouse, France, pp 415−422.

Larson, S. D. Phase studies of the two-component carbon dioxide-water systems involving the carbon dioxide hydrate. Ph.D. Thesis, University of Illinois at Urbana-Champaign, IL, 1955.

Mei, D.-H.; Liao, J.; Yang, J.-T.; Guo, T.-M. Experimental and modeling studies on the hydrate formation of a methane + nitrogen gas mixture in the presence of aqueous electrolyte solutions. *Ind. Eng. Chem. Res.* **1996**, *35*, 4342−4347.

Mei, D.-H.; Liao, J.; Yang; J.-T.; Guo, T.-M. Hydrate formation of a synthetic natural gas mixture in aqueous solutions containing electrolyte, methanol, and (electrolyte + methanol). *J. Chem. Eng. Data* **1998**, *43*, 178−182.

Ng, H. J.; Robinson, D. B. Hydrate formation in systems containing methane, ethane, propane, carbon dioxide or hydrogen sulfide in the presence of methanol. *Fluid Phase Equilib.* **1985**, *21*, 145−155.

Parent, J. S. Investigation in to the nucleation behavior of the clathrate hydrates of natural gas components. M.Sc. Thesis, Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada, 1993.

Robinson, D. B.; Mehta, B. Hydrates in the propane-carbon dioxide-water system. *J. Can. Pet. Technol.* **1971**, *10*, 33−35.

Saji, A.; Yoshida, H.; Sakai, M.; Tanii, T.; Kamata, T.; Kitamura, H. Fixation of carbon dioxide by clathrate-hydrate. *Energy Convers. Manage.* **1992**, *33* (5−8), 643−649.

Tohidi, B.; Danesh, A.; Todd, A. C.; Burgass, R. W. Hydrate-free zone for synthetic and real reservoir fluids in the presence of saline water. *Chem. Eng. Sci.* **1997**, *52*, 3257−3263.

Unruh, C. H.; Katz, D. L. *Trans. ASME* **1949**, *186*, 83.

Zuo, Y.-X.; Gommesen, S.; Guo, T.-M. *Chin. J. Chem. Eng.* **1996**, *4* (2), 189−202.

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