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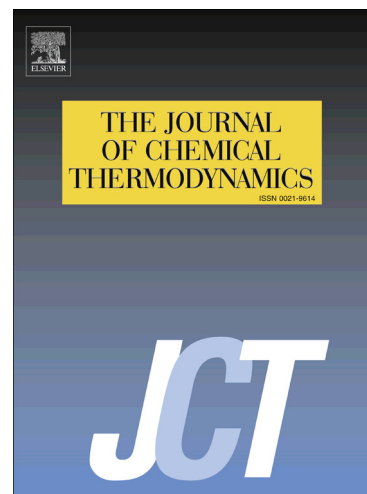
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Phase equilibrium measurements for clathrate hydrates of flue gas (CO₂ + N₂ + O₂) in the presence of tetra-n-butyl ammonium bromide or tri-n-butylphosphine oxide

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Abstract This paper reports the measured hydrate phase equilibria of simulated flue gas (12.6 vol% CO₂, 80.5 vol% N₂, 6.9 vol% O₂) in the presence of tetra-n-butyl ammonium bromide (TBAB) or tri-n-butylphosphine oxide (TBPO), at 0 wt%, 5 wt%, and 26 wt%, respectively. The measurements of the phase boundary between hydrate-liquid-vapor (H-L-V) phases and liquid-vapor (L-V) phases were performed within the temperature range (275.97 - 293.99) K and pressure range (1.56 - 18.78) MPa with using the isochoric step-heating pressure search method. It was found that addition of TBAB or TBPO allowed the incipient equilibrium hydrate formation conditions for the flue gas to become milder. Compared to TBAB, TBPO was largely more effective in reducing the phase equilibrium pressure.

Keywords: Semi-clathrate hydrate; Phase equilibrium; Carbon dioxide capture; Hydrate promoter; Gas separation.

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1. Introduction

CO₂ emission from coal fired power stations is among the major contributors to global warming [1, 2]. There is a pressing need to develop safe, cost-effective technologies to capture CO₂ from fossil fuel combustion [3]. Despite the satisfactory separation efficiency of current CO₂ capture methods, a challenge remains as to how to reduce the cost and achieve high regenerability [3, 4]. One of the most promising attempts for addressing this challenge is CO₂ hydrate formation [5-12]. CO₂ hydrate is one of gas hydrates that are inclusion compounds with cages formed by the hydrogen-bonded water molecules and guest species [13]. One can employ the differences in the hydrate phase equilibrium conditions of CO₂ [14], O₂ [15] and N₂ [15] to selectively engage CO₂ into the cages of hydrate [16] while leaving other gas molecules behind. However, gas hydrate formation in water generally requires high working pressure; there is a need for lowering the pressure requirement in order to improve the process safety and lower the cost.

One demonstrated method for lowering the pressure requirement for hydrate formation is to use chemical additives. Chemicals such as Tetrahydrofuran (THF) and cyclopentane (CP) are capable of reducing the equilibrium pressure [17-19] but the high volatility of these chemicals is undesirable. A group of additives, known as semi-clathrate hydrate (SCH) formers or ionic hydrate formers, are nonvolatile and can lead to lower pressure requirement than THF and CP [20, 21]. In these SCH crystalline solids, CO₂, CH₄, H₂, or other gas molecules can be trapped in dodecahedral cavities (5¹²), along with larger cavities composed of water and anions encaging the cations with covalent bonded alkyl chains [22]. Shimada et al. [23] and Kamata et al. [24] investigated SCHs formed from tetra-n-butyl ammonium bromide (TBAB) and showed that the unoccupied cages in these SCHs could trap suitably sized molecules and thus can be used as a vehicle for storing and separating gases. SCHs

have drawn increasing interest for their potential applications in gas storage [25-27] and gas separation [28-30].

Table 1. Phase equilibrium measurements for clathrate hydrates of binary mixture of (CO₂ + N₂) with or without additives.

Authors	CO ₂ content in the feed gas / mol%	Additives	Additive mass fraction/ wt%
Fan et al. [34]	90.99, 96.52	-	-
Kang et al. [32]	6.63, 11.59, 17.61, 48.15, 77.8, 96.59	-	-
	17, 70	THF	3.89, 11
Bruusgaard et al. [36]	0, 21, 50, 80, 100	-	-
Bouchafaa et al. [39]	10, 30, 50, 75	-	-
		TBAB	10, 30, 40
Kim et al. [38]	84.1, 90.6	-	-
Sfaxi et al. [37]	27.1, 47.6, 74.8, 77.3, 81.2	-	-
		TBAB	40
Lu et al. [41]	15.9	-	-
		THF	1.077, 3.89, 10.77, 14.29
		TBAB	5, 15.3, 34.8, 40.7, 45.7
Meysel et al. [31]	20, 50, 75	TBAB	5, 10, 20
Mohammadi et al. [21]	15.1, 39.9	TBAB	5, 15, 30

- denotes no additives

Phase equilibrium measurements are an important step toward elucidating the phenomena of gas enclathration, optimizing the thermodynamic models, and developing effective CO₂ capture processes.

The incipient hydrate formation conditions of binary mixture of CO₂ and N₂ has been extensively studied [16, 21, 31 - 41], and Table 1 lists the feed gas compositions and chemical additives used in phase equilibrium measurements. The chemical additive predominately used in these studies was TBAB or THF. Note also that O₂ was absent in the feed gas mixture studied by others, who assumed

that O₂ has the same performance as N₂ in enclathration. In the present work, we measured the hydrate phase equilibrium conditions of ternary mixture of CO₂, N₂ and O₂, representing the flue gas from Australian coal-fired power stations [42 - 44], in the presence and absence of TBAB or Tri-n-butylphosphine Oxide (TBPO). TBPO is a less known SCH former and with water, it could form both TBPO·28H₂O and TBPO·34.5H₂O SCHs under atmospheric pressure, with the melting point being 279.65 and 280.25 K, respectively [45, 46]. The latter TBPO hydrate (corresponding to 26 wt% TBPO aqueous solution) with a higher melting point has a crystal unit composed of four 5¹²6⁴ cages, four 5¹²6³ cages, four 5¹²6² cages, and fourteen 5¹² cages associated with 148 H₂O in hydrate structure, and the unoccupied 5¹² cages can engage small gas molecules [45]. The present work was carried out with the purpose of understanding the effects of additive type and concentration on the phase equilibrium conditions of flue gas.

2. Experimental

2.1. Materials

TBAB and TBPO used in the present work were supplied by Sigma-Aldrich. Simulated flue gas was obtained from Coregas Pty Ltd. All of these materials were used as received. Deionized water was used to prepare the aqueous solutions of TBPO or TBAB. The specifications of the materials used in the experiments are listed in Table 2.

Table 2 Specifications of the materials used in the experiments.

Sample name	Chemical formula	Supplier	Composition ^a
TBAB	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	Sigma-Aldrich	0.99 mass fraction
TBPO	[CH ₃ (CH ₂) ₃] ₃ P(O)	Sigma-Aldrich	0.95 mass fraction

	CO ₂		0.126 mole fraction
Simulated flue gas	N ₂	Coregas Pty Ltd	0.805 mole fraction
	O ₂		0.069 mole fraction

^a No further purification was done before use.

2.2. Experimental apparatus

The schematic diagram of the experimental apparatus and its details can be found elsewhere [47, 48]. Briefly, the high pressure reactor used in the present work was a home-made non-visual 102 ml stainless steel cylindrical vessel with inside diameter of 38 mm and depth of 90 mm. The vessel was immersed in a liquid bath, which was connected to a temperature control circulator. A gas booster was used to feed the pressurized flue gas into the vessel. A magnetically driven stirrer with rotating speed of 600 rpm was used to agitate the test liquid in the vessel. A thermowell coupled with a matched 1/10 DIN ultra precise immersion RTD sensor was inserted into the reactor to measure the liquid or hydrate phase temperature with an uncertainty of ± 0.03 K. A pressure transducer with accuracy of ± 0.01 MPa was used to measure the gas pressure inside the reactor. The experimental data were collected using a data acquisition system at 10-second intervals.

2.3. Experimental procedure

The high pressure vessel was cleaned at least seven times with using deionized water and dried prior to the introduction of TBAB or TBPO aqueous solution. The test solution was then loaded into the vessel. A vacuum pump (Javac CC-45) was used to degas the entire system with its effect on the concentration of the test solution being negligible. The hydrate phase equilibrium measurements were performed at the temperature range of (275.97 - 293.99) K and pressure range (1.56 - 18.78) MPa with using the isochoric equilibrium step-heating pressure search method.

Figure 1 shows typical pressure-temperature traces, from which the hydrate dissociation point can be determined [13]. In the present work, the uncertainty for determining the hydrate dissociation point was ± 0.01 MPa and ± 0.1 K.

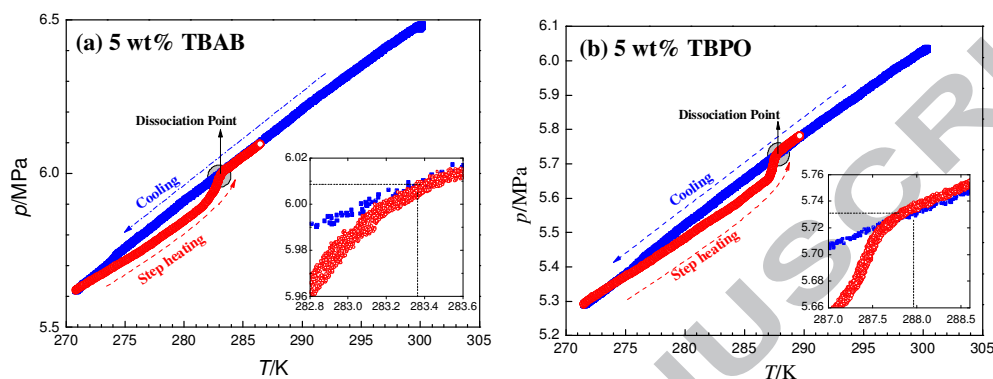


Figure 1. Determination of hydrate dissociation point of flue gas from pressure-temperature trace: (a) 5 wt% TBAB; (b) 5 wt% TBPO.

3. Results and Discussion

The reliability and accuracy of our experimental system have been described in our recent work [47]. In the present work, the phase equilibrium conditions of flue gas + water are tabulated in Table 3 and plotted in Figure 2.

Figure 2 shows the phase equilibrium conditions of the flue gas hydrate in the absence of additives. Also plotted in this figure are the phase equilibria of simple hydrates of N_2 , O_2 , and CO_2 , for comparison. As shown, the equilibrium pressure increased with increasing temperature. At a given temperature, the equilibrium pressure of the flue gas hydrate was lower than N_2 and O_2 hydrates but was higher than that of CO_2 hydrate. This result is consistent with the fact that CO_2 hydrate is thermodynamically more stable than N_2 and O_2 hydrates. However, the measured incipient hydrate formation pressure for flue gas is prohibitively high and needs to be significantly decreased for hydrate-based technology applications. In what follows, two additives TBAB and TBPO were

respectively tested for their effects on hydrate phase equilibrium conditions, and the results are tabulated in Table 4 and plotted in Figures 3 and 4, respectively.

Table 3. Phase Equilibrium Data of Flue Gas Hydrate in Deionized Water.

Flue Gas + H ₂ O	
T/K^a	p/MPa^b
276.0	8.49
277.1	11.52
278.1	14.21
279.0	17.17

^a Standard uncertainty on temperature $u(T) = 0.1$ K

^b Standard uncertainty on pressure $u(p) = 0.01$ MPa.

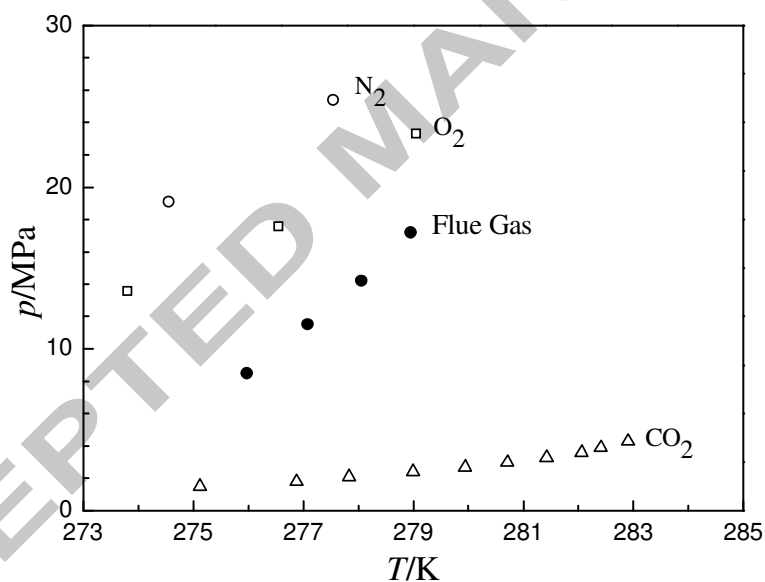


Figure 2. Hydrate phase equilibrium conditions of N₂, O₂, CO₂, and flue gas (12.6 vol% CO₂, 80.5 vol% N₂, 6.9 vol% O₂). ○, N₂, ref [15]; □, O₂, ref [15]; △, CO₂, ref [19]; •, Flue Gas, this work.

Table 4. Phase Equilibrium Data of Flue Gas Hydrate with TBAB or TBPO solutions, at two initial loadings.

Flue Gas + H ₂ O + TBAB			
5 wt%		26 wt%	
T/K^a	p/MPa^b	T/K^a	p/MPa^b
281.5	2.67	285.6	1.63
283.4	6.01	286.9	3.84
284.8	9.91	288.6	7.32
286.7	14.13	290.4	11.69
288.4	18.78	291.8	17.41
Flue Gas + H ₂ O + TBPO			
5 wt%		26 wt%	
T/K^a	p/MPa^b	T/K^a	p/MPa^b
283.8	2.26	284.1	1.56
288.0	5.73	287.4	4.08
290.3	9.35	290.6	8.54
292.3	14.09	292.6	13.29
293.9	18.47	294.0	18.14

^a Standard uncertainty $u(T) = 0.1$ K

^b Standard uncertainty $u(p) = 0.01$ MPa

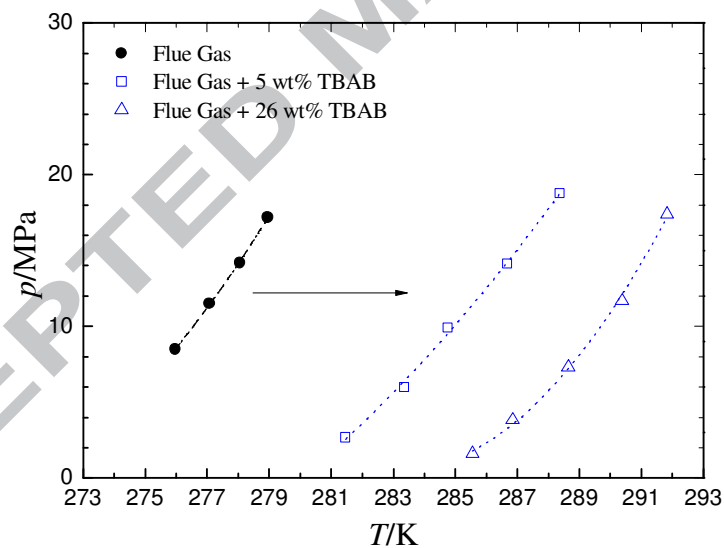


Figure 3. Hydrate phase equilibrium conditions for flue gas measured at different TBAB

concentrations. The lines are drawn to guide the eye.

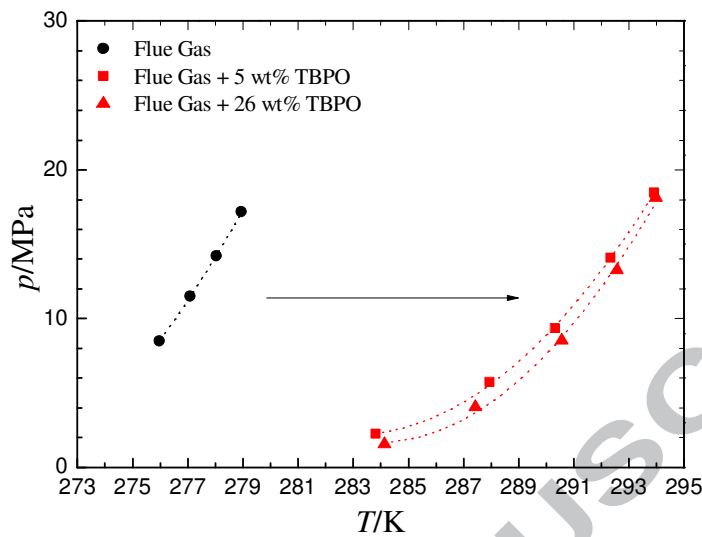


Figure 4. Hydrate phase equilibrium conditions for flue gas measured at different TBPO concentrations. The lines are drawn to guide the eye.

Figures 3 and 4 respectively show that addition of TBAB and TBPO considerably shifted the phase equilibrium curves to the lower right region. Specifically, at 5 MPa, increasing TBAB concentration from 5 wt% to 26 wt% would increase the hydrate phase equilibrium temperature from 283 K to 288 K, that is, a 5-K shift. In contrast, increasing TBPO concentration from 5 wt% to 26 wt% would see only a 1-K shift. The above observation made for flue gas hydrates at high pressures was consistent with the observation made at 0.1 MPa that the difference in the dissociation temperature between 40.8 wt% TBAB (corresponding to TBAB·26H₂O) and 32 wt% TBAB (TBAB·38H₂O) was relatively large (i.e. 5 K) [49] whereas the difference between 30.2 wt% TBPO (TBPO·28H₂O) and 26.0 wt% TBPO (TBPO·34.5H₂O) was rather small (less than 1 K) [45, 46]. Moreover, the measured dissociation temperature of 5 wt% TBPO at ambient pressure was 276.2 K (with uncertainty of 0.5 K), whereas the corresponding temperature of 5 wt% TBAB was estimated by extrapolation to be 274.8 K

or lower, depending on the hydrate type [40].

Figure 5 compares the effects of TBPO and TBAB on lowering the pressure requirement for flue gas hydrate formation. With an initial reagent loading of 5 wt%, at any given temperature under study, the TBPO SCHs had much lower phase equilibrium pressure than TBAB SCHs. With an initial reagent loading of 26 wt%, the TBPO SCHs had slightly lower phase equilibrium pressure than TBAB SCHs at temperature above 287 K. Below 287 K, however, TBAB appears to be more effective than TBPO in reducing the hydrate equilibrium pressure of flue gas. Overall, TBPO seems more effective than TBAB in reducing the phase equilibrium pressure.

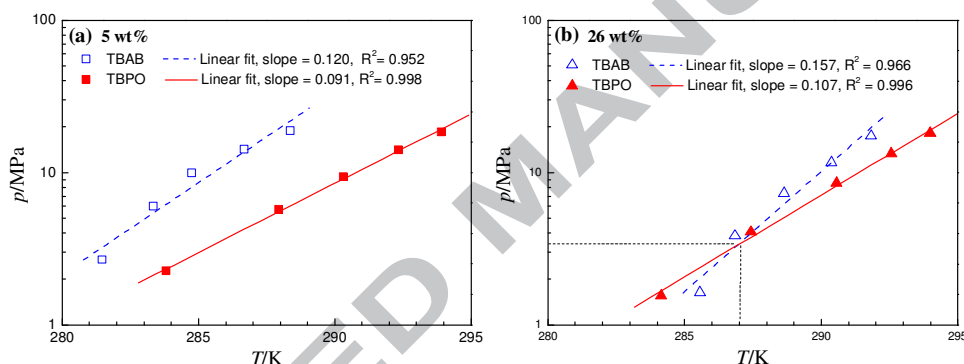


Figure 5. Comparison between TBAB and TBPO at different concentrations: (a) 5 wt% and (b) 26 wt%. The lines represent the best linear fits to the experimental data (see Table 4).

In Figure 5, the semi-logarithmic plots of p and T can be considered reflecting the Clausius-Clapeyron plots ($\ln p$ versus $1/T$, not shown here) since within a narrow temperature range (270 – 300 K), there is a strong linear relationship between $1/T$ and T , with $R^2 > 0.999$. It was found that the R^2 values of the linear fits for TBAB were lower than those for TBPO, and the slopes of the linear fits for TBAB curves were larger than those of TBPO, implying different energetics of dissociation of flue gas hydrates with TBAB and TBPO.

4. Conclusions

The phase equilibrium conditions of simulated flue gas (12.6 vol% CO₂, 80.5 vol% N₂, 6.9 vol% O₂) in the presence of deionized water and the aqueous solutions of TBAB or TBPO at 5 wt% and 26 wt% were measured in the temperature range of (275.97-293.99) K and pressure range (1.56-18.78) MPa. It was found that addition of TBAB or TBPO allowed the dissociation conditions of flue gas hydrate to shift to higher temperatures and lower pressures. The semi-clathrate hydrates of TBPO + flue gas are generally more stable thermodynamically than that of TBAB + flue gas. At a given temperature, the equilibrium pressures of the semi-clathrate hydrates decreased noticeably with increasing initial TBAB loading from 5 to 26 wt%, but only minor changes were seen with the corresponding increase in initial TBPO loading. At 5 wt%, TBPO performed better than TBAB in reducing the equilibrium pressure over the entire temperature range under study. At 26 wt%, TBPO outperformed TBAB in reducing the equilibrium pressure at temperature above 287 K.

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References

- [1] B. Metz, O. Davidson, H. De Coninck, M. Loos, L. Meyer, IPCC, Cambridge University Press: Cambridge, United Kingdom and New York, USA, 2005.
- [2] S. Aparicio, M. Atilhan, The Journal of Physical Chemistry C 117 (2013) 15061-15074.
- [3] D. Aaron, C. Tsouris, Separation Science and Technology 40 (2005) 321-348.

- [4] M. Balsamo, F. Rodríguez-Reinoso, F. Montagnaro, A. Lancia, A. Erto, *Ind Eng Chem Res* 52 (2013) 12183-12191.
- [5] A. Eslamimanesh, A.H. Mohammadi, D. Richon, P. Naidoo, D. Ramjugernath, *Journal of Chemical Thermodynamics* 46 (2012) 62-71.
- [6] Y.-T. Seo, I.L. Moudrakovski, J.A. Ripmeester, J.-w. Lee, H. Lee, *Environ Sci Technol* 39 (2005) 2315-2319.
- [7] S. Fan, S. Li, J. Wang, X. Lang, Y. Wang, *Energy Fuel* 23 (2009) 4202-4208.
- [8] Y. Wang, X. Lang, S. Fan, *Journal of Energy Chemistry* 22 (2013) 39-47.
- [9] A. Adeyemo, R. Kumar, P. Linga, J. Ripmeester, P. Englezos, *Int J Greenh Gas Con* 4 (2010) 478-485.
- [10] P. Babu, R. Kumar, P. Linga, *Energy* 50 (2013) 364-373.
- [11] P. Linga, R. Kumar, J.D. Lee, J. Ripmeester, P. Englezos, *Int J Greenh Gas Con* 4 (2010) 630-637.
- [12] C.-G. Xu, Z.-Y. Chen, J. Cai, X.-S. Li, *Energy Fuel* (2013).
- [13] E.D. Sloan, C.A. Koh, *Clathrate Hydrates of Natural Gases*, Third Edition, CRC Press, Taylor & Francis, New York, 2008.
- [14] M.M. Mooijer-van den Heuvel, R. Witteman, C.J. Peters, *Fluid Phase Equilib* 182 (2001) 97-110.
- [15] A.H. Mohammadi, B. Tohidi, R.W. Burgass, *Journal of Chemical & Engineering Data* 48 (2003) 612-616.
- [16] J.M. Herri, A. Bouchemoua, M. Kwaterski, A. Fezoua, Y. Ouabbas, A. Cameirao, *Fluid Phase Equilib* 301 (2011) 171-190.
- [17] S.P. Kang, H. Lee, C.S. Lee, W.M. Sung, *Fluid Phase Equilib* 185 (2001) 101-109.
- [18] B. Tohidi, A. Danesh, A.C. Todd, R.W. Burgass, K.K. Ostergaard, *Fluid Phase Equilib* 138 (1997)

241-250.

[19] K.M. Sabil, G.-J. Witkamp, C.J. Peters, *The Journal of Chemical Thermodynamics* 42 (2010)

8-16.

[20] M. Arjmandi, A. Chapoy, B. Tohidi, *J Chem Eng Data* 52 (2007) 2153-2158.

[21] A.H. Mohammadi, A. Eslamimanesh, V. Belandria, D. Richon, P. Naidoo, D. Ramjugernath,

Journal of Chemical Thermodynamics 46 (2012) 57-61.

[22] D.L. Fowler, W.V. Loebenstein, D.B. Pall, C.A. Kraus, *J Am Chem Soc* 62 (1940) 1140-1142.

[23] W. Shimada, T. Ebinuma, H. Oyama, Y. Kamata, S. Takeya, T. Uchida, J. Nagao, H. Narita,

Japanese Journal of Applied Physics Part 2-Letters 42 (2003) L129-L131.

[24] Y. Kamata, H. Oyama, W. Shimada, T. Ebinuma, S. Takeya, T. Uchida, J. Nagao, H. Narita,

Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers 43

(2004) 362-365.

[25] N.H. Duc, F. Chauvy, J.-M. Herri, *Energ Convers Manage* 48 (2007) 1313-1322.

[26] J. Deschamps, D. Dalmazzone, *Journal of Chemical & Engineering Data* 55 (2010) 3395-3399.

[27] A.A. Sizikov, A.Y. Manakov, T.V. Rodionova, *Energ Fuel* 26 (2012) 3711-3716.

[28] J. Gholinezhad, *Experimental investigation of semi-clathrate hydrates with application towards*

gas storage, transportation and separation, PhD thesis, Heriot-Watt University, 2012.

[29] M. Ricaurte, C. Dicharry, D. Broseta, X. Renaud, J.P. Torre, *Ind Eng Chem Res* 52 (2013)

899-910.

[30] T.E. Rufford, S. Smart, G.C.Y. Watson, B.F. Graham, J. Boxall, J.C.D. da Costa, E.F. May, *J*

Petrol Sci Eng 94-95 (2012) 123-154.

[31] P. Meysel, L. Oellrich, P. Raj Bishnoi, M.A. Clarke, *The Journal of Chemical Thermodynamics* 43

- (2011) 1475-1479.
- [32] S.-P. Kang, H. Lee, *Environ Sci Technol* 34 (2000) 4397-4400.
- [33] S. Li, S. Fan, J. Wang, X. Lang, Y. Wang, *Chinese J Chem Eng* 18 (2010) 202-206.
- [34] S.-S. Fan, T.-M. Guo, *Journal of Chemical & Engineering Data* 44 (1999) 829-832.
- [35] P. Linga, R. Kumar, P. Englezos, *J Hazard Mater* 149 (2007) 625-629.
- [36] H. Bruusgaard, J.G. Beltrán, P. Servio, *Journal of Chemical & Engineering Data* 53 (2008) 2594-2597.
- [37] I.B.A. Sfaxi, V. Belandria, A.H. Mohammadi, R. Lugo, D. Richon, *Chem Eng Sci* 84 (2012) 602-611.
- [38] S.H. Kim, M.D. Seo, J.W. Kang, C.S. Lee, *Fluid Phase Equilib* 306 (2011) 229-233.
- [39] W. Bouchafaa, D. Dalmazzone, *Proceedings of the 7th International Conference on Gas Hydrates*, 2011, 17-21.
- [40] J. Deschamps, D. Dalmazzone, *J Therm Anal Calorim* 98 (2009) 113-118.
- [41] T. Lu, Y. Zhang, X.S. Li, Z.Y. Chen, K.F. Yan, *Guocheng Gongcheng Xuebao/The Chinese Journal of Process Engineering* 9 (2009) 541-544.
- [42] E. Meuleman, Y. Artanto, J. Jansen, M. Osborn, P. Pearson, A. Cottrell, P. Feron, 6th International Technical Conference on Clean Coal & Fuel Systems, 2010.
- [43] A.J. Cottrell, J.M. McGregor, J. Jansen, Y. Artanto, N. Dave, S. Morgan, P. Pearson, M.I. Attalla, L. Wardhaugh, H. Yu, A. Allport, P.H.M. Feron, *Energy Procedia* 1 (2009) 1003-1010.
- [44] P. Cook, *International journal of environmental studies* 63 (2006) 731-749.
- [45] V.I. Alekseev, Y.V. Gatilov, T.M. Polyanskaya, V.V. Bakakin, Y.A., Dyadin, L.A. Gaponenko, *J. Struct. Chem.* 23 (1982) 395-399.

[46] Y.A. Dyadin, K. Udachin, J. Struct. Chem. 28 (1987) 394-432.

[47] J. Du, L. Wang, Ind Eng Chem Res 53 (2014) 1234-1241.

[48] J. Du, H. Li, L. Wang, Ind Eng Chem Res 53 (2014) 8182-8187.

[49] H. Oyama, W. Shimada, T. Ebinuma, Y. Kamata, S. Takeya, T. Uchida, J. Nagao, H. Narita, Fluid

Phase Equilibr 234 (2005) 131-135.

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Table 4. Phase Equilibrium Data of Flue Gas Hydrate with TBAB or TBPO solutions, at two initial loadings.

Flue Gas + H ₂ O + TBAB			
5 wt%		26 wt%	
<i>T</i> /K ^a	<i>p</i> /MPa ^b	<i>T</i> /K ^a	<i>p</i> /MPa ^b
281.5	2.67	285.6	1.63
283.4	6.01	286.9	3.84
284.8	9.91	288.6	7.32
286.7	14.13	290.4	11.69
288.4	18.78	291.8	17.41
Flue Gas + H ₂ O + TBPO			
5 wt%		26 wt%	
<i>T</i> /K ^a	<i>p</i> /MPa ^b	<i>T</i> /K ^a	<i>p</i> /MPa ^b
283.8	2.26	284.1	1.56
288.0	5.73	287.4	4.08
290.3	9.35	290.6	8.54
292.3	14.09	292.6	13.29
293.9	18.47	294.0	18.14

^a Standard uncertainty $u(T) = 0.1$ K

^b Standard uncertainty $u(p) = 0.01$ MPa

Highlights:

- Semi-clathrate hydrate phase equilibria for ternary gas mixture of CO₂, N₂, and O₂ are reported;
- An isochoric pressure-search method was used;
- TBPO outperforms TBAB in promoting the formation of flue gas hydrate.

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