Phase Equilibria and Methane Enrichment of Clathrate Hydrates of Mine Ventilation Air + Tetrabutylphosphonium Bromide

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ABSTRACT: This paper reports the experimentally measured phase equilibrium conditions for the clathrate hydrates formed from simulated mine ventilation air (0.50 vol% CH_4 + 99.50 vol% air) in the presence of 0, 5, 20, 37.1 and 50 wt% of Tetrabutylphosphonium Bromide (TBPB). These equilibrium conditions were measured at the temperature range of (281.62 to 292.49) K and pressure range of (1.92 to 18.55) MPa by using an isochoric equilibrium step-heating pressure search method. The results showed that addition of TBPB allowed the hydrate dissociation condition for mine ventilation air to become milder and at a given temperature, the lowest hydrate dissociation pressure was achieved at 37.1 wt% TBPB, corresponding to the stoichiometric composition for $TBPB\cdot 32H_2O$. For each TBPB concentration tested, the semilogarithmic plots of hydrate dissociation pressure versus reciprocal absolute temperature can be satisfactorily fitted to two straight lines intersecting at 6.5 MPa. The slopes of these fitted straight lines are indifferent to changes in TBPB concentration. Gas composition analysis by gas chromatography also found that in the presence of 37.1 wt% TBPB, CH_4 could be enriched approximately 3.5-fold in the hydrate phase.

1. INTRODUCTION

Fossil fuels will continue to be the primary energy source in the foreseeable future. CO_2 generated from fossil fuel combustion needs to be captured and sequestrated. There are many technical options for separation and/or capture of CO_2 from combustion flue gas and other industrial effluents.[1] However, relatively little attention is paid to capture of methane, which has approximately twenty-one times higher greenhouse effect than carbon dioxide. Capture of fugitive methane is attractive environmentally as well as providing a potential energy source.[2] One of the major sources of fugitive methane is the dilute methane emitted from coal mine ventilation shafts, known as mine ventilation air (MVA). MVA is most difficult to use as an energy source as the air volume is large and the methane resource is dilute and variable in concentration, generally less than 1.0 vol% methane (typically around 0.3 - 0.5 vol%).[3,4] There is a clear need for enriching methane from low levels up to requirements of lean-burn methane utilisation technologies (e.g. 1.0 vol% CH_4 for CSIRO system,[5] 1.6 vol% CH_4 for Carburetted Gas Turbine system,[6] and 2.0 vol% CH_4 for Kawasaki Turbine system[7]).

The most common attempted methods for capturing methane from MVA include adsorption (solvent adsorption, temperature swing adsorption, pressure swing adsorption) and separation (cryogenic separation and membrane separation).[8] These methods are expensive or ineffective for capturing methane from MVA and may suffer from the negative impact of water vapor and particulate contaminations. Gas hydrate crystallization with a lattice of hydrogen bonded water molecules encaging small gaseous molecules such as CO_2 or CH_4 is a promising method for carbon capture and sequestration.[9-11] For MVA, it involves converting methane into hydrate and keeping the other gases in gaseous form, thereby allowing methane to be separated from others. The equilibrium formation pressure of CH_4 hydrate is much lower than those of N_2 and O_2 hydrates at the same temperature.[12,13] Therefore, CH_4 enters the hydrate phase preferentially and can be recovered from the CH_4-N_2-O_2 gas mixture after hydrate decomposition.[14] Despite its compelling advantages, hydrate formation generally requires high pressure (usually above 5 MPa) at room ambient temperature.

A group of additives, known as semi-clathrate hydrate (SCH) formers or ionic hydrate formers, can remarkably lower pressure requirement for hydrate formation.[15] A typical SCH former is tetra-n-butyl ammonium bromide (TBAB), which is capable of reducing the hydrate formation pressure and is extensively investigated for storing and separating gases.[11, 16-22] TBAB has also been examined for its potential to separate methane from coal methane gas.[23, 24] However, the methane concentrations in these studies were relatively high, over 25 vol%. Only one theoretical study undertaken by Adamova et al.[25] reports the hydrate formation pressure of coal mine gas with dilute methane (0.5 vol% CH_4, 75 vol% N_2 and 24.5 wt% O_2) and suggests that it might be possible to upgrade methane from MVA using gas hydrate technology.

Another SCH former, tetrabutylphosphonium Bromide (TBPB) has recently drawn intention from researchers because of its higher gas storage capacity than TBAB and similar capability of reducing hydrate formation pressure.[18, 26, 27] One of the stoichiometric compositions for TBPB hydrate is $TBPB\cdot 32H_2O$, which has ten 5^{12} small cages, sixteen $5^{12}6^2$ and four $5^{12}6^3$ cages per unit cell.[28, 29] Recently, the SCH stability conditions of TBPB with pure gases such as CO_2,[26, 30-33] H_2,[18] CH_4[20, 26] and N_2[26, 32] have been reported, and the experimental conditions are summarized in Table 1. These results show the possibility of capturing CH_4 from the MVA at proper thermodynamic conditions by using gas hydrate technology in the presence of TBPB. To the best of our knowledge, neither experimental measurements of the thermodynamic conditions of TBPB + MVA semi-clathrate hydrates nor experimental investigations on the potential viability and efficiency of this separation process have been reported. In the present work, we systematically report the phase equilibrium conditions of MVA + TBPB SCHs and analyze the gas composition in the hydrate whose initial formation pressure is relatively low. These data are essential for technology development for recovering CH_4 from MVA by gas hydrate crystallization.

2. EXPERIMENTAL

2.1. Materials

TBPB (powder, 98 wt% pure) was purchased from Sigma-Aldrich. Simulated ventilation air methane (0.50 vol% CH_4 + 99.50 vol% air) was obtained from Coregas. All of these materials were used as received. Deionized water was used to prepare the aqueous solutions of TBPB.

2.2. Experimental apparatus

The experimental apparatus used for phase equilibrium condition measurements in the present work was the same as in our previous study.[34] Briefly, a home-made non-visual 102 ml stainless steel cylindrical vessel with inside diameter of 38 mm and inside depth of 90 mm was used as the hydrate reactor. The reactor was immersed in a liquid bath, which was connected to a temperature control circulator (Haake A25). A thermowell coupled with a matched 1/10 DIN ultraprecise immersion RTD sensor (Omega) was inserted into the reactor to measure the liquid or hydrate phase temperature with an uncertainty of ± 0.03 K. A pressure transducer (Omega part number MMA5.0KC1P1C2T4A6CE) with accuracy of ± 0.01 MPa was used to measure the gas pressure inside the reactor. A magnetically driven stirrer with rotating speed of 600 rpm was used to agitate the test liquid. The gas discharged from a gas booster outlet was fed into the reactor. The experimental data were collected using a data acquisition system (Agilent 34970A) at 10 s intervals.

A 362.5 ml stainless steel vessel (Model BR300, Berghof) was used to prepare the MVA semiclathrate hydrate samples for gas composition analysis. More details on this vessel can be found in our previous study.[36] The gas composition analysis was carried out using a gas chromatograph (GC, Shimazu model GC-2014), which is equipped with Alltech Washed Molesieve 5A 80/100 column, with ultra-high purity Argon used as carrier gas.

2.3. Experimental procedure

The hydrate phase equilibrium measurements were carried out as follows. First, the 102 ml high pressure cell was cleaned at least seven times with using deionized water and dried prior to introduction of TBPB aqueous solution. The test solution (40 g) was then loaded into the clean and dry reactor. A vacuum pump (Javac CC-45) was used to degas the entire system except the reactor for 5 to 10 minutes. Subsequently, the test solution in the reactor was degassed for 0.5 - 1 minute before undergoing hydrate experiments. The effect of degassing on the concentration of the test solution was negligible. The hydrate dissociation condition measurements were performed at the temperature range of (281.62 to 292.49) K and pressure range of (1.92 to 18.55) MPa with using the same isochoric equilibrium step-heating pressure search method as in our previous work.[34] Figure 1 shows a typical pressure-temperature trace (for 5 wt% TBPB solution + MVA SCH), from which the dissociation point was determined to be 288.51 K and 18.39 MPa. The maximum uncertainties for determining the hydrate dissociation temperatures and pressures were 0.1 K and 0.01 MPa, respectively, which are comparable to the measuring uncertainties reported by Mohammadi and Richon.[35]

The MVA semiclathrate hydrate samples for gas composition analysis were formed from 75 ml solution in the 362.5 ml vessel with stirring rate of 600 rpm at 278 K and initial pressure 4 MPa. After a sufficiently long period for the hydrate formation to be complete (indicated by gas pressure having remained constant for more than 3 hours), the GC was used to measure the gas composition of the co-existing vapor phase in the headspace. Then the vapor phase was completely evacuated from the reactor by using a vacuum pump, followed by dissociation of the hydrate at elevated temperature for releasing the trapped gas, whose composition was measured by the GC. For each gas sample, at least three readings were taken and their average was recorded. All the gas samples were collected using Tedlar gas sample bags (0.5 liter, SKC). Before sampling, the sample bags were degassed by the vacuum pump for 1 – 2 minutes and rinsed with the sample gas 3 – 4 times.

3. RESULTS AND DISCUSSION

The reliability of our experimental system was given in detail in a previous communication of ours,[34] which shows excellent agreement between our phase equilibrium data of TBAB + H_2O +

N_2 or CH_4 and those reported by other research groups. In the present work, the measured phase equilibrium conditions of MVA SCHs at 0, 5, 20, 37.1 and 50 wt% TBPB are tabulated in Tables 2 and 3 and plotted in Figure 2. For comparison, the phase equilibrium conditions of air hydrate[13] are also plotted in Figure 2. As shown, the equilibrium pressure increased with increasing temperature. At a given temperature, the equilibrium pressure of MVA hydrate without chemical additives was lower than that of air hydrate, suggesting that 0.5 vol% CH_4 had a stabilizing effect on air hydrate. This result is consistent with the fact that CH_4 hydrate is thermodynamically more stable than N_2 and O_2 hydrates.[37]

At a given temperature, the equilibrium pressure of MVA hydrate in the absence of any chemical additives was substantially higher than that of MVA + 5 wt% TBPB SCHs. Increasing TBPB concentration from 0 to 20 wt% noticeably shifted the phase equilibrium curve to the lower right region. However, increasing TBPB concentration from 20 to 37.1 wt% shifted the phase equilibrium curve to the right only slightly, and further increase in TBPB concentration to 50 wt% brought the curve back slightly, indicating that the overly dosed TBPB would have less effective in reducing the pressure requirement for MVA hydrate formation. Overall, the hydrate equilibrium conditions were less sensitive to changes in TBPB concentration in the range of 20 to 50 wt% than those in the range of 0 to 20 wt%, and the most thermodynamically stable equilibrium condition was obtained at 37.1 wt% TBPB. Similar observation was made by other workers for the hydrate phase equilibrium conditions of N_2 + TBPB solution.[32]

When reporting the hydrate phase equilibrium data of a gas mixture, one should consider reporting the composition of the gas in the headspace of the reactor under hydrate equilibrium condition.[38,39] In this work, the phase equilibrium data were reported with the assumption that the composition of the simulated MVA sourced from the gas cylinder was the same as that in the reactor under hydrate dissociation condition because there was large volume of gas in the headspace of the reactor, and the solubility of CH_4 and air in water would be exceedingly low and close to each other. Final proof for this assumption would require measurements of the solubility of CH_4 and air in TBPB solutions.

Comparison of hydrate dissociation conditions in TBPB + MVA, CH_4 or N_2 systems was made and presented in Figure 3 by the semilogarithmic plot of semi-clathrate hydrate phase equilibrium pressure ($\ln P$) versus reciprocal temperature ($1/T$). As a first approximation, these SCH systems can be considered roughly complying with the requirement of the Clausius–Clapeyron equation, and the energetics of SCH dissociation can be inferred by the slope of the straight lines fitted to $\ln P$ versus $1/T$ data. The equilibrium data reported in ref 33 for N_2 + TBPB SCHs (above 7 MPa) can be satisfactorily fitted to straight lines with the same slope, irrespective of TBPB concentration (see Figure 3a), suggesting that the concentration of TBPB has little influence on the enthalpy of hydrate dissociation. The $\ln P$ versus $1/T$ plots made from the equilibrium data (below 5 MPa) adapted from ref 26 can be satisfactorily fitted by two straight lines intersecting at 1.8 MPa for the N_2 + 35 wt% TBPB SCH and 0.8 MPa for the CH_4 + 35 wt% TBPB SCH. Likewise, the equilibrium data for MVA + TBPB SCHs obtained in the present work can be satisfactorily fitted to two straight lines crossing over each other at 6.5 MPa, at all TBPB concentrations tested. Overall, the heat of dissociation seemed smaller at higher pressures, which could be attributed to an occupation change of guest gas molecules in the empty cages of these SCHs. According to Sloan and Koh[36], the approximate heat of dissociation should be relevant to cavity occupation, and less energy is required to dissociate structures with more cavities filled than those with fewer cavities filled. The above slope change might also be linked to a possible hydrate structure transition induced by the pressure change, which points to the need for further work with applying suitable techniques such as Raman spectroscopy or X-ray to examine the hydrate structure at different pressures.

To verify the potential viability of the hydrate-based separation method for methane capture from MVA with TBPB, we measured the gas composition (CH_4, N_2, and O_2 content, on a water-free basis) of the hydrate phase formed from 75 ml 37.1 wt% TBPB solution at 278 K (subcooling was 8.5 K) and initial pressure 4 MPa. The experiment was repeated independently. Table 4 shows that the hydrate phase had an average CH_4 content of 1.75 vol%, with standard deviation of 0.05 vol%. This CH_4 content was 3.5 times higher than that of the feed gas (i.e., 0.50 vol%), suggesting that CH_4 was substantially enriched in the hydrate phase and that it is promising to separate methane from MVA by clathrate hydrate crystallization aided by TBPB. Further work is under way to improve the selectivity and efficiency of this process and the results will be reported in the next communication.

Note that the O_2 content in the MVA semiclathrate hydrate phase was also higher than in the feed gas, in contrast to the decreased N_2 content. This finding is in coincidence with the reported substantial oxygen enrichment in the natural air hydrate formed in Arctic and Antarctic ice sheets[40,41] and synthetic air hydrate[42,43] probably owing to the preferential occupation of small cavities by O_2 in air hydrate.[44] Air hydrates usually form a type II crystal structure, which is built from 8 large and 16 small cages per unit cell, and nitrogen and oxygen contained in the air enter into these cages.[45] Pure nitrogen and oxygen also form structure II hydrates whereas pure methane forms structure I hydrate, which is built from 6 large and 2 small cages per unit cell.[17] It is reported that TBAB semiclathrate hydrate can only incorporates gas molecules that fit in the empty small cage.[46] It is, therefore, possible that MVA semiclathrate hydrates formed from TBPB solutions might also incorporate the gases in the small cages alone. Further work with applying suitable techniques such as Raman spectroscopy is needed to understand the cage filling. The observed enrichment of CH_4 and O_2 in the MVA semiclathrate hydrate phase could be attributed to the higher affinity of CH_4 and O_2 to the small cages than that of N_2. At 273.15 K, for ordinary gas hydrates, the dissociation pressures of CH_4 and O_2 hydrates are almost 13 and 4 MPa lower than that of N_2 hydrate, respectively.[26,37] Likewise, at a given temperature and TBPB concentration, the dissociation pressure of CH_4 + TBPB semiclathrate hydrate is much lower than that of N_2 + TBPB semiclathrate hydrate.[26,32]

4. CONCLUSIONS

The phase equilibrium conditions of SCHs formed from mine ventilation air in the presence of at 0, 5, 20, 37.1 and 50 wt% TBPB were measured in the temperature range of (281.62 to 292.49) K and pressure range of (1.92 to 18.55) MPa. It was found that addition of TBPB moved the MVA hydrate equilibrium conditions to higher temperatures and lower pressures, and the most thermodynamically stable TBPB + MVA SCH was obtained at 37.1 wt%. The hydrate equilibrium conditions were relatively indifferent to changes in TBPB concentration from 20 to

50 wt%. For each TBPB concentration tested, the semilogarithmic plots of hydrate dissociation pressure versus reciprocal absolute temperature can be satisfactorily fitted to two straight lines crossing over each other at 6.5 MPa. The slopes of these fitted straight lines are indifferent to changes in TBPB concentration. It was also found that in the presence of 37.1 wt% TBPB, CH_4 was preferentially incorporated into the hydrate phase and the enrichment was approximately 3.5-fold, suggesting that a hydrate-based method is promising for separating methane from MVA.

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FIGURE CAPTIONS

Figure 1. Determination of hydrate dissociation point from a typical pressure-temperature trace.

Figure 2. Phase equilibrium data of MVA in the presence of TBPB at different concentrations: ○, deionized water (0 wt%); ■, 5 wt%; ▲, 20 wt%; ●, 37.1 wt%; ╳**,** 50 wt%. ◇, air + deionized water (adapted from ref 13). The lines are drawn to guide the eye.

Figure 3. Semilogarithmic plot of semi-clathrate hydrate phase equilibrium pressure versus reciprocal phase equilibrium temperature: (a) pure gases; (b) MVA.

Table 1. Experimental Conditions for SCHs of gases + TBPB.

Authors	wt%$_{TBPB}$	Guest gas	T/K	P/MPa
Mayoufi et al.[30]	37.1	CO_2	(281.1 to 289)	(0.5 to 2)
Deschamps et al.[18]	37.1	H_2	(285 to 287.2)	(12.1 to 23.3)
Mayoufi et al.[31]	(5 to 60)	CO_2	(284.6 to 288.5)	(0.5 to 1.7)
Gholinezhad[20]	37	CH_4	283.15	0.1
Suginaka et al.[26]	35	CO_2, CH_4, N_2	(282.6 to 291.6)	(0.15 to 5.1)
Shi et al.[32]	5, 10, 37.1, 60	CO_2, N_2	(282.2 to 292.0)	(1.32 to 16.86)
Zhang et al.[33]	10, 20, 35, 50	CO_2	(281.0 to 292.0)	(0.4 to 4.0)

Table 2. Phase Equilibrium Data of MVA Hydrate in the Absence of Chemical Additives.

Simulated Ventilation Air Methane + H_2O	
T/K ± 0.1	P/MPa ± 0.01
276.79	16.91
277.22	17.99

Table 3. Phase Equilibrium Data of MVA in the Presence of TBPB at Different Concentrations.

MVA + TBPB + H_2O							
5 wt%		20 wt%		37.1 wt%		50 wt%	
T/K ± 0.1	P/MPa±0.01	T/K± 0.1	P/MPa±0.01	T/K± 0.1	P/MPa±0.01	T/K± 0.1	P/MPa±0.01
281.62	1.92	285.05	2.52	285.26	1.99	285.3	2.57
282.99	4.62	285.85	3.81	287.45	5.57	286.77	5.08
285.13	9.31	288.18	8.14	289.68	9.96	288.41	8.11
286.96	14.18	290.35	13.77	291.41	14.48	290.49	12.87
288.51	18.39	292.02	18.55	292.49	18.33	292.22	18.12

Table 4. Composition of gases (on a water-free basis) in different phases[a]

	CH_4 (vol%)	N_2 (vol%)	O_2 (vol%)
Hydrate phase	1.75 ± 0.05	72.4 ± 0.3	25.5 ± 0.2
Co-existing gas phase	0.45 ± 0.05	79.4 ± 1.4	19.9 ± 0.8

[a] Feed gas composition = 0.50 vol% CH_4 + 78.6 vol% N_2 + 20.9 vol% O_2

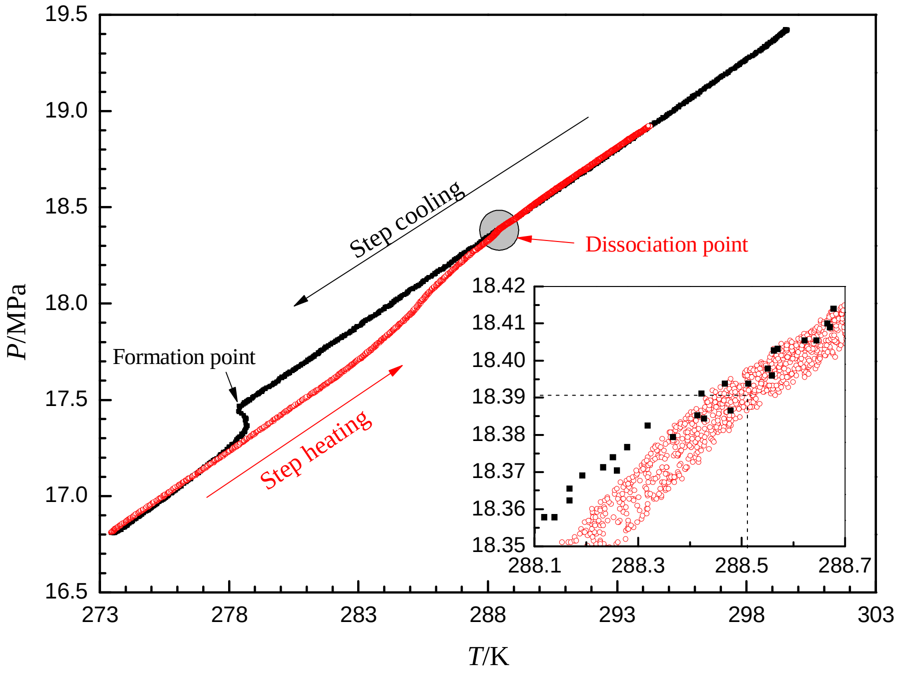


Figure 1. Determination of hydrate dissociation point from a typical pressure-temperature trace.

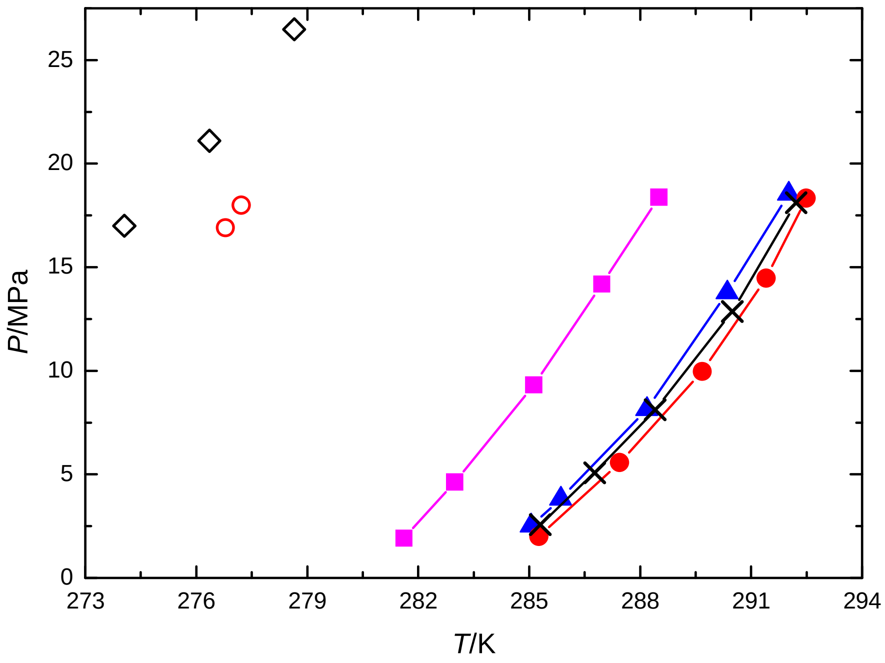
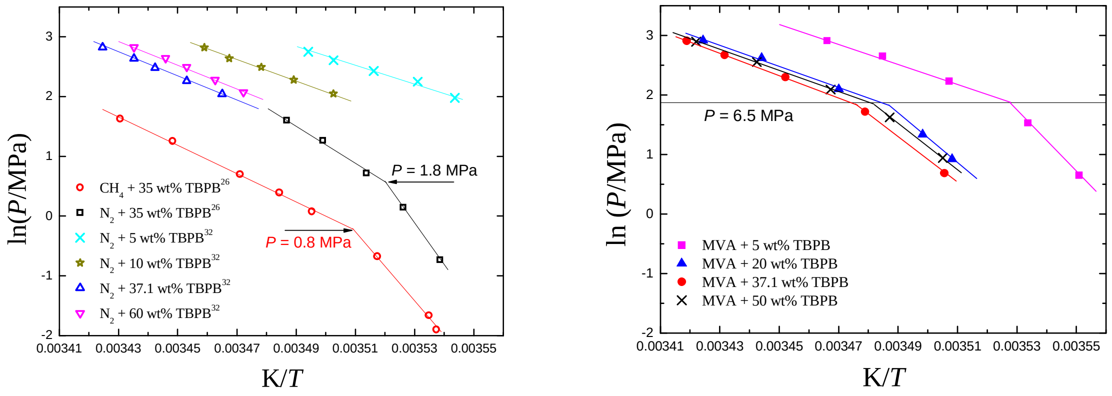


Figure 2. Phase equilibrium data of MVA in the presence of TBPB at different concentrations: ○, deionized water (0 wt%); ■, 5 wt%; ▲, 20 wt%; ●, 37.1 wt%; ╳, 50 wt%. ◇, air + deionized water (adapted from ref 13). The lines are drawn to guide the eye.



(a) (b)

Figure 3. Semilogarithmic plot of semi-clathrate hydrate phase equilibrium pressure versus reciprocal phase equilibrium temperature: (a) pure gases; (b) MVA.

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