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Experimental studies on methane hydrates with thermodynamic promoter molecules

Deepala V.S.G.K.Sharma[1], **Vangala Dhanunjana Chari**[1,2], **Pinnelli S.R.Prasad**[1]*

[1]Gas Hydrates Division, National Geophysical Research Institute, Council of Scientific and Industrial Research, Hyderabad-500007, (INDIA)

[2]Department of Physics, Osmania University, Hyderabad-500007, (INDIA)

ABSTRACT

A systematic study on methane hydrate (MH) formation and dissociation was carried out in the presence of liquid hydrocarbon promoter molecules namely Tetrahydrofuran (THF), *tert*-Butylamine (*t*-BuNH$_2$) and Trimethylamine (TMA). The observed methane gas consumption least (0.944g for *t*-BuNH$_2$ and to 1.648g for pure MH) was consistent with the hydrate structure with two guest (CH$_4$ & promoter) molecules. The kinetic promotion effect has been studied; methane hydrate formation rate was much faster in case of THF (110 minutes) than *t*-BuNH$_2$ (300 minutes) and the thermodynamic promoter effect on MH was maximum for THF and minimum for *t*-BuNH$_2$.

KEYWORDS

Clathrate hydrates;
Tetrahydrofuran;
Tert-Butyl amine;
Trimethylamine;
Methane hydrtate formation and dissociation.

INTRODUCTION

Gas hydrates (clathrates) are the non-stoichiometric inclusion compounds where gaseous guest molecules are trapped in a host lattice formed by water molecules in an ice-like hydrogen-bonded framework. Hydrates exist as a stable solid phase at high gas pressures and/or low temperatures. Three distinct structural families, termed structures I, II, and H, are known, characterized by distinct size and shape of the polyhedral cages that capture guest molecules according to their structures. The amount of fuel (natural) gas stored in this form is extremely high depending on the available vacant cages in a hydrogen-bonded water network. There are five types of hydrate cages commonly found in increasing size: pentagonal dodecahedron (5^{12}-cage), dodecahedron ($4^{3}5^{6}6^{3}$-cage), tetrakaidecahedron ($5^{12}6^{2}$-cage), hexakaidecahedron ($5^{12}6^{4}$-cage), and icosahedron ($5^{12}6^{8}$-cage). The three common unit cells (sI, sII and sH) of gas hydrates are known to form from a few types of hydrate cages depending largely on the size and physical properties of the guest species. For example, sI can host small molecules such as methane, ethane and carbon dioxide, while sII can host larger molecules such as propane and isobutane. The cubic sI unit cell contains 46 H_2O molecules, two 12-hedra (5^{12}), and six 14-hedra ($5^{12}6^{2}$); where 5^{12} indicate that the polyhedron contains 12 five-member ring faces. The cubic sII cell contains 136 water molecules, eight large ($5^{12}6^{4}$), and sixteen small (5^{12}) cages. The sH hydrate consists of three different cages: three 5^{12}-cages, two $4^{3}5^{6}6^{3}$-cages and one $5^{12}6^{8}$-cage[1].

Gas hydrates have been of a particular concern for the oil and gas industry because the operating conditions of oil and gas production pipelines are conducive for the formation of gas hydrates, resulting in blockage of pipelines[2–5]. However, studies on gas hydrate have greatly evolved because of not only the concern on production pipelines but also the great potential of these hydrates as a source of natural gas, as massive deposits exist both under the permafrost and in sediments of continental margins. Gas hydrates also represent an attractive way of storing large quantities of gas, such as hydrogen[6–11], natural gas[4,12–14], and carbon dioxide[4,15]. Extensive efforts are in progress to develop efficient storage techniques in both the scientific and industrial fields, although to date there has been little effort made to understand the physical properties of gas hydrates formed from multi-components of natural gas. The gas separation processes by hydrate formation often demands suitable pressure and temperature conditions[4,16–19]. Another important application of gas hydrates is in the refrigeration processes[4]. Storage and transportation of fuel gases like methane and hydrogen in the form of gas hydrates is advantageous because of its safety, higher volumetric yield, and lower production costs compared with conventional storage methods like liquefaction[4]. But methane hydrates normally are stable under high pressure and subzero temperatures, their formation kinetics and temperature, pressure of hydrate formation is also a concern[4]. Thus not convenient for storage/ transportation applications; in order to overcome these difficulties aforementioned thermodynamic promoter molecules are used. The disadvantage with such multi-component hydrate forming systems is that the promoter molecules themselves are the "guests" in hydrate systems and thus the storage capacity of a fuel gas such as methane is reduced. However, advantage is that the hydrate formation may take place at lower pressures & higher temperatures compared to pure (methane) hydrates.

The unit cell structure of THF hydrates is sII (*Fd3m - cubic*) with eight $5^{12}6^4$ cages occupied by THF molecules and there are sixteen 5^{12} vacant cages which could possibly be occupied by methane molecules in mixed hydrates[20]. The unit cell structure for *t*-BuNH$_2$ hydrate is sVI ($I\bar{4}3d - cubic$) with sixteen ($4^35^96^27^3$) cages occupied by *t*-BuNH$_2$ and twelve (4^45^4) cages are vacant[21]. Recent studies have demonstrated that the sVI structure of *t*-BuNH$_2$ clathrates is highly unstable upon pressurizing with suitable gas (CH_4 or H_2) to fill the vacant 4^45^4 cages[22,23]. Experimental studies by Kim et.al.[23] and Prasad et.al.[9,22] clearly established the structure of mixed (with more than one guest molecules) hydrate system as sII. The use of trimethylamine (TMA) as a promoter molecule is interesting because the clathrate system with TMA is reported to have higher stability conditions[10,24]. The unit-cell (*P6/mmm - hexagonal*) of TMA hydrates has different cages; three 5^{12}, two $4^25^86^3(6)^2$ and two $5^6(5)^66^1(6)^1$ cages; these are semi-clathrates with the later two types of cages being occupied by a larger guest molecule (TMA)[24]. In mixed hydrates the second guest can occupy the vacant 5^{12} cages[10].

In this article we reported methane hydrate formation & dissociation characteristics under identical experimental conditions such as stirring rate, rate of temperature variation and initial methane pressure etc, in the presence of THF, *t*-BuNH$_2$ and TMA molecules. We also have compared the methane gas storage capacity in hydrates using these promoter molecules.

EXPERIMENTAL METHOD

Materials

Aqueous solutions were prepared following the gravimetric method using an METLER TOLEDO (AB104-S) high accuracy analytical balance. Consequently, uncertainties on mole fractions are estimated to be below 0.01. The source and purity of various liquid promoters used in this study were tabulated in TABLE 1.

TABLE 1 : Samples utilized with their purity and suppliers

Sample	Purity	Supplier
Tetra Hydro Furan (THF)	98%	Qualigens fine chemicals, India
t-Butyl amine (*t*-BuNH$_2$)	98%	Sigma Aldrich, Germany
Tri Methylamine (TMA)	25 wt % in water	SAFC Supply Solutions, Germany
water	Doubly distilled and deionised water	

Experimental section

Briefly, the main part of the apparatus is a SS-316 cylindrical vessel, which can withstand pressures up to 10 MPa. The volume of the vessel is 100 ml. A stirrer with variable speed was installed in the vessel to agitate the fluids and hydrate crystals formed inside. All the experiments were conducted at a fixed speed of 500 rpm and the stirrer was kept on throughout the experimental run. Cold fluid (water + glycol mixture) was circulated around the vessel with the help of LAB COMPANION (RW-0525G) circulator, to maintain the temperature inside it at a desired level. A platinum resistance thermometer (Pt100) was inserted into the vessel and used for measuring the temperatures within ± 0.2°. Pressure in the vessel was measured with a WIKA pressure transducer (WIKA, type A-10 for pressure range 0 to16 MPa). Doubly distilled, de-ionized and degassed water was used for hydrate formations. The reactor was filled with 30 – 40 ml of water/ stock solution with required mole fraction of promoter molecules.

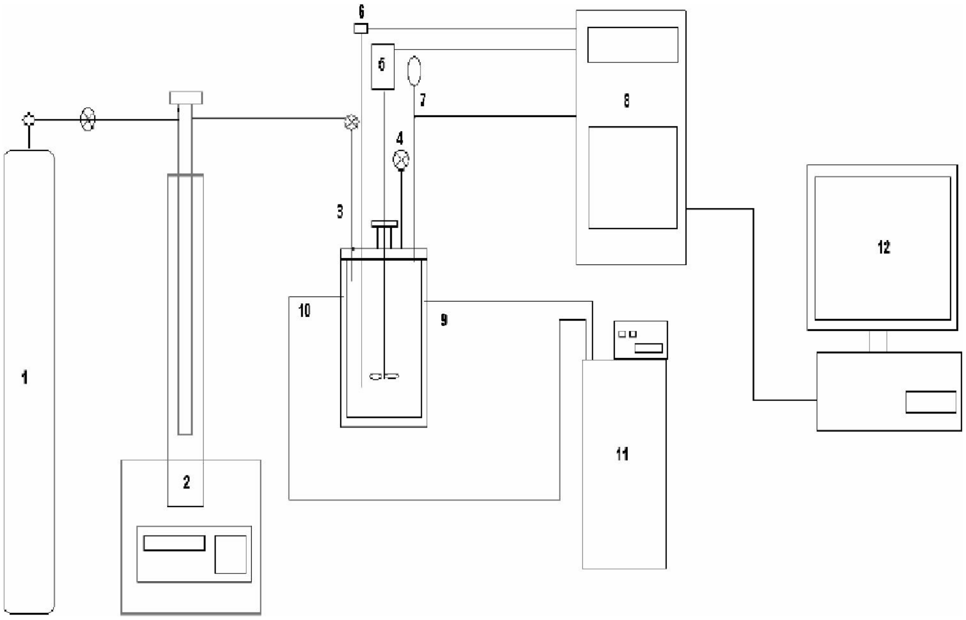

Figure 1 : Schematic diagram of the experimental setup. 1. CH_4 Gas cylinder, 2. ISCO Pump, 3. Inlet port for Gas, 4. Outlet/ Vacuum port, 5. Magnetic Stirrer assembly, 6. Temperature sensor, 7. Pressure gauge and transducer, 8. Data acquisition and control, 9. Inlet for cold fluid, 10. Outlet for cold fluid, 11. Closed cycle refrigerant fluid circulator (LAB CHAMPION) and 12. Computer.

Equilibrium conditions were measured by the isochoric pressure search method[25]. The vessel containing an aqueous solution (approximately 40% by volume of the vessel) was immersed into the temperature controlled bath, and gas was supplied to the desired level from a cylinder using the TELEDYNE ISCO Syringe pump (Model 100DX). Note that the vessel was evacuated before introducing any aqueous solution and gas. After obtaining temperature and pressure stability (preferably away from the hydrate formation pressure for a specific temperatures), the valve inline connecting the vessel and the ISCO pump/cylinder was closed (Figure 1). Subsequently, temperature was slowly decreased to allow the system to form the hydrates. Typical rate of cooling from point a to b; b to c & c to d respectively is 0.1, 0.002 & 0.3 K/min (see in Figure 2B). Hydrate formation in vessel was detected by the pressure drop. During the process of dissociation, the temperature was increased in steps of 1° per hour. At each step, temperature was kept constant with sufficient time to achieve an equilibrium state. In this way, a pressure - temperature diagram was obtained for each experimental run. If the temperature is increased in the hydrate-forming region, there was a partial dissociation of hydrate crystals, thereby substantially increasing the pressure. An increase in temperature outside the hydrate region shows a smaller increase in the pressure, as a result of the change in the phase equilibrium of the fluids. Consequently, the point at which the slope of pressure-temperature data plots changed sharply was considered to be the point at which all hydrate crystals were dissociated. It is known from literature that stirring rate affects the formation kinetics and above some rate it has effect on the induction times but do not have effect on mass and heat transfer[26,27].

RESULTS AND DISCUSSIONS

The equilibrium pressure and temperatures for stable phases like liquid hydrate (H), water (L_w) and vapor (V) have discernible variation in the P-T trajectory. The promoters like THF[25] or *t*-$BuNH_2$[28] were used in the hydrate formation to alleviate the thermodynamics and/ or kinetic processes[29]. It is evident that the methane hydrate formation at given pressure occurred at higher temperatures in the presence of promoter molecules. During the start and at the end of the experiment the methane molecules (in moles) in the reactor were estimated from:

n = (PV/ZRT)

where the compressibility factor '*Z'* was referred from Perry's Chemical Engineers' Handbook (Methane Z Compressibility Factor, page 172), 'V' is the volume of the gas phase in the reactor and 'R' is the gas constant. Pressure (P) and Temperature (T) were logged at a fixed time intervals.

In TABLE 2, the amount of H_2O and the promoter used in various experimental runs and the amount of methane consumption from the gas phase due to hydrate formation was tabulated. Consumed methane in mole fraction ($n_{CH4}/n_{Hydrate}$) is calculated from the decrement of methane (in vapour phase) to the total of water and liquid promoters (in moles) used in each experimental run. The observed consumption of methane from vapour was in pure hydrate is $x = 0.060$, whereas, the expected mole fraction for hydrate with sI structure ($8{\cdot}CH_4\ 46{\cdot}H_2O$) is 0.150. The amount of hydrate conversion is calculated as the ratio of consumed methane gas mole fraction from the experiments to the one from ideal structural composition and the same for pure methane hydrates was 39.28%. In Figure 2, we show the methane content in vapor phase (in m.mol) & temperature (*T*) variations with time during the hydrate formation. Corresponding cycle pressure – temperature ($p - T$) trajectories (in both hydrate formation & dissociation stages) are shown in the inset. We conducted methane hydrate formation and dissociation with aqueous solutions of THF($x = 0.060$), tBA ($x = 0.061$ & 0.093) and TMA ($x = 0.088$) under identical conditions. Pure methane hydrate (without using any promoter) shows slow hydrate formation, the arrow mark in Figure 1A indicates that it takes around 500 minutes to complete maximum hydrate formation (approximately 90%) and compared with the phase boundary curve of sI methane hydrate was generated using CSMGEM shown as continuous line in pressure – temperature trajectory (inset of Figure 2A), Which is far higher than THF ($x = 0.060$), for which almost total hydrate formation completed in just 120 minutes. From Figure 2B it is clearly seen that there is fairly good agreement between the observed and computed dissociation behaviour and the hydrate conversion was higher in mixed hydrates with THF. The mixed hydrates formed under these conditions are of structure sII, with THF molecules in $5^{12}6^4$ cages, while CH_4 molecules are enclathrated in 5^{12} cages[30]. The observed consumption of methane from vapour was in aqueous THF ($x = 0.060$) is $x = 0.050$, whereas, the expected mole fraction for hydrate with sII structure ($8{\cdot}CH_4\ 17{\cdot}H2O\ 136{\cdot}H_2O$) is 0.100. THF acts as a better kinetic promoter and completes methane hydrate formation in just 120 minutes (much faster than in pure methane hydrate). The amount of hydrate conversion is calculated as the ratio of consumed methane gas mole fraction from the experiments to the one from ideal structural composition and the same for pure methane hydrates was 49.77% (TABLE 2).

The *t*-$BuNH_2$ is another promoter which has got high potential for fuel gas storage; however, the critical issue is regarding the stability of cubic sVI structure of pure *t*-$BuNH_2$ clathrates[9]. Recent studies have clearly demonstrated that the sVI was highly unstable in mixed hydrates it transformed into sII upon pressurizing with a suitable gas to populate vacant cages[9,22,23]. We have conducted the experiments using both 0.093 and 0.061 mole fractions of *t*-$BuNH_2$ as they represent the stoichiometric amounts for sVI and sII respectively. In the aqueous solution of *t*-$BuNH_2$ ($x = 0.061$) observed methane consumption was ~0.050 and this correspond to hydrate conversion 48.52%, which is comparable to THF (see TABLE 2), and the major hydrate formation completes in 300minutes whereas in in sVI composition it takes 130 minutes. The observed methane consumption for sVI stoichiometry is just 0.037 (much lower than sII composition), resulting into hydrate conversion of 56.87 %. However, following earlier studies[9,22,23] one cannot consider the structure for mixed hydrates as sVI but it should be sII and thus the true hydrate

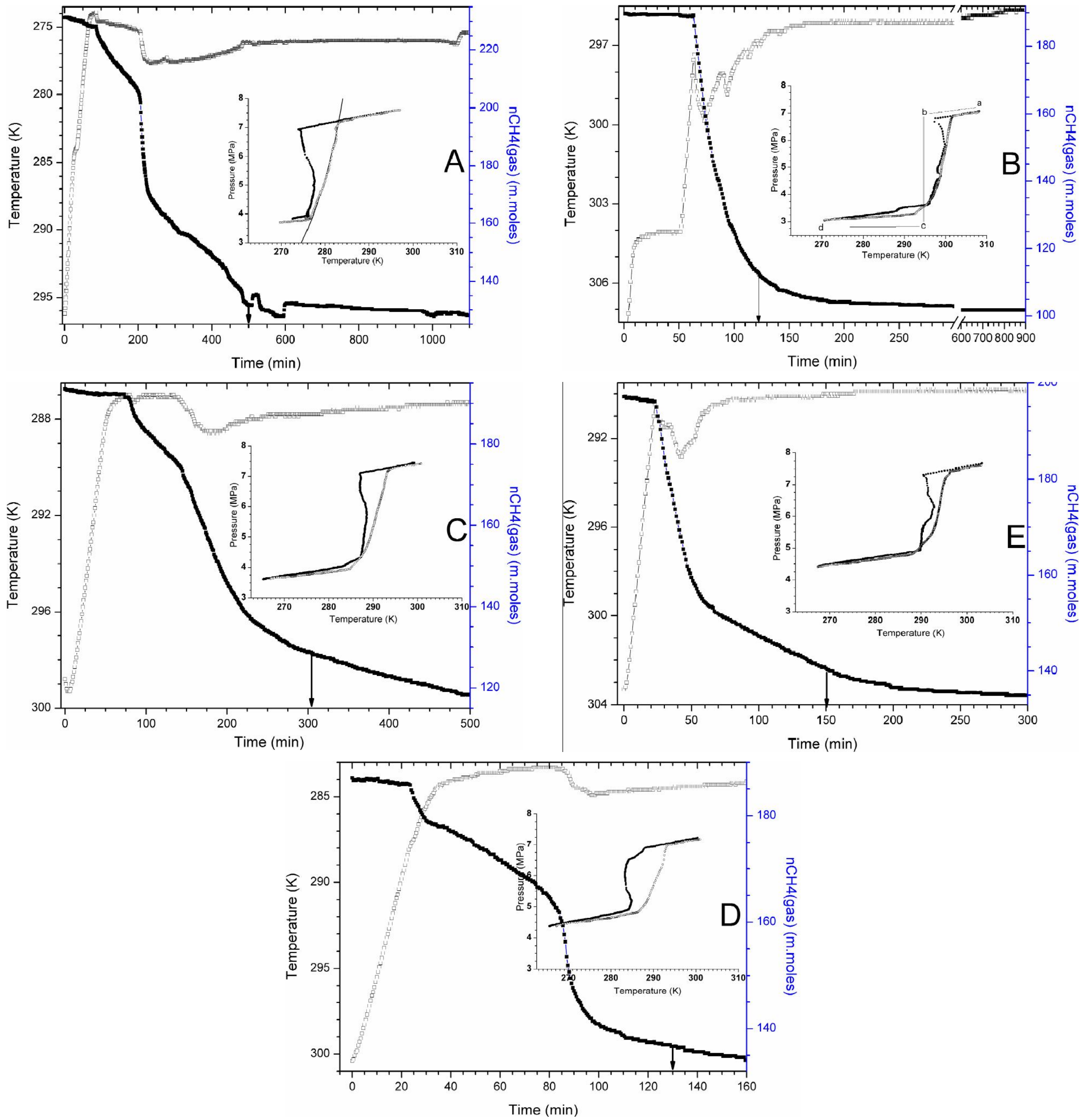

Figure 2 : Kinetics of formation and in sub diagram formation and dissociation of methane hydrate (MH) with water (A), and aqueous solutions of 0.060 mole fraction of tetrahydrofuran (THF) (B); 0.061 mole fraction of *tert*-Butylamine (*t*-BuNH$_2$) (C) ; 0.093 mole fraction of (*t*-BuNH$_2$) (D) and 0.088 mole fraction of trimethylamine (TMA) (E). Filled and open symbols respectively represent the observed behavior during cooling and warming cycles. The continuous line in sub diagram of A represents the phase boundary for sI – MH calculated using CSMGEM program.

conversion from these experiments was recalculated as 37.09 %. Further the hydrate formation in aqueous *t*-BuNH$_2$ solution with 0.093 mole fraction occurred at about 3° lower than that of 0.061 mole fraction (see inset of Figure 2C & 2D), while no appreciable drift in the dissociation behavior was observed (see in Figure 3b & c). Liang et. al., also reported no variation in the phase stability behavior for mixed hydrates of methane with *t*-BuNH$_2$ mole fractions (0.097 & 0.056), whereas, the phase boundary for mixed hydrates with lower *t*-BuNH$_2$ mole fraction (0.01) shifted to lower temperature side[28]. Addition of more tBA to sII composition enhances the formation rate but decreases the methane consumption (0.944 g). This result corroborates earlier statement that “*excess t-BuNH$_2$ inhibits hydrate formation in a mixed hydrate system*”[23,31].

TABLE 2 : Table describes the preparation of methane hydrates with different thermodynamic promoters and all the experiments carried out with constant stirring speed (500 rpm). Observed and Expected CH_4 mole fraction during the hydrate formation with % yield are also tabulated.

Sample (mole fraction)	Preparation		CH_4 gas Consumed	Mole fraction of CH_4 in Hydrate ($n_{CH4}/n_{Hydrate}$)		% yield
	H_2O	Promoter		Expected [a]	Observed	
Pure MH	30g	–	1.648g	0.150	0.060	39.28
THF (0.060)	31g	7.974g	1.536g	0.100	0.050	49.77
t-BuNH$_2$ (0.061)	29g	7.656g	1.400g	0.100	0.050	48.52
t-BuNH$_2$ (0.093)	25g	10.440g	0.944g	0.065	0.037	56.87, [b] 37.09, [c]
TMA (0.088)	27.96g	9.320g	0.960g	0.063	0.034	54.20

Another promoter system that we used was trimethylamine (TMA) and this is an interesting system in the sense that the clathrates with TMA (0.088 mole fraction) reported to have higher stability[8,22] (see Figure 2E). However, this system forms semi-clathrates and the TMA molecules occupy different large cages (two- $4^2 5^8 6^3 (6)^2$ and two- $5^6 (5)^6 6^1 (6)^1$) and also are part of network formation by having H-bonding with water molecules. The three vacant 5^{12} cages in the unit-cell could be occupied by CH_4 molecules. As shown in TABLE 2, the hydrate conversion was around 54.20 % for TMA system. Figure 2E shows that TMA is a better kinetic promoter like THF, which completes formation (90 % of hydrate conversion) in just 150 minutes. The observed consumption of methane from vapour was in semi clathrate hydrate formation is $x = 0.034$, whereas, the expected mole fraction for hydrate with semi clathrate structure ($3{\cdot}CH_4\ 4{\cdot}TMA\ 41{\cdot}H_2O$) is 0.063. The amount of hydrate conversion is calculated as the ratio of consumed methane gas mole fraction from the experiments to the one from ideal structural composition and the yield was 54.20 % (see in TABLE 2).

In Figure 3, we show the pressure of methane gas evolved as the hydrates dissociated due to an increment in temperature inside the reactor. We observed a close match between the experimental and computed phase boundary using CSMGEM for pure methane hydrate system (Figure 3a). It is evident that the mixed hydrates of CH_4 with THF dissociates (Figure 3e) at a much higher temperature (~18°) compared to pure methane hydrates. Our data also closely match with the literature data[32]. The so called “promoter effect” for methane hydrates was lower for mixed hydrates with *t*-BuNH$_2$. Both hydrate systems with *t*-BuNH$_2$ (0.061 & 0.093 mole fractions) have similar dissociation patterns. The dissociation curve for mixed hydrate system with TMA is mid-way to THF and *t*-BuNH$_2$ (0.061 mole fraction). Thus, from our studies it could be concluded that promoter effect on MH among the mixed hydrate systems decreases in the following order:

CH_4+THF (0.060 mole fraction) > CH_4+TMA (0.088 mole fraction) > CH_4+ *t*-BuNH$_2$ (0.093 mole fraction) e” CH_4+ *t*-BuNH$_2$ (0.061 mole fraction) > CH_4

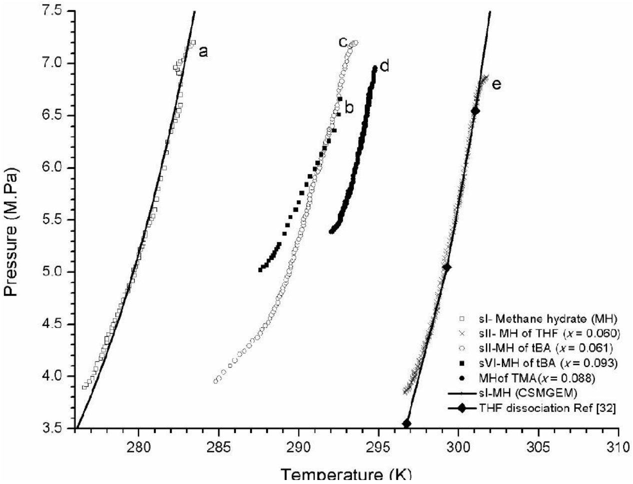

Figure 3 : Dissociation temperatures and pressures of Methane hydrates prepared by different Thermodynamic promoters: Pure methane hydrate - a, methane hydrates of aqueous solutions of *t*-BuNH$_2$ (0.061 mole fraction) – b, *t*-BuNH$_2$ (0.093 mole fraction) – c, TMA (0.088 mole fraction) – d, THF (0.060 mole fraction) – e. The continuous line represents the phase boundary for sI – MH calculated using CSMGEM program (at ‘a’) and literature data [32] of THF dissociation (at ‘e’).

CONCLUSIONS

Methane hydrate formation/ dissociation studied under identical experimental conditions in the presence water soluble solvents namely Tetrahydrofuran (THF), *tert*-Butylamine (*t*-BuNH$_2$) and Trimethylamine (TMA). Hydrate formation kinetics are tremendously increased by using these promoters. Clathrates formed by these thermodynamic promoters dissociate at higher temperatures than pure methane hydrate, for THF around 18°, TMA 13° and *t*-BuNH$_2$ 11°. Among these promoters THF shows a high thermodynamic promoter affect than other two.

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