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Phase equilibrium measurements for semi-clathrate hydrates of the ($CO_2 + N_2$ + tetra-n-butylammonium bromide) aqueous solution systems: Part 2

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ABSTRACT

Equilibrium pressures for dissociation of the carbon dioxide (CO_2) + nitrogen (N_2) + tetra-n-butylammonium bromide (TBAB) + semi-clathrate (sc) hydrates have been experimentally measured to determine the stability regions and dissociation conditions of mixed $CO_2 + N_2$ + TBAB semi-clathrate hydrates. Semi-clathrates have been formed with the addition of TBAB aqueous solutions with mass fractions of (0.05 and 0.30). The relative molar fractions of CO_2 in the feed gas were (0.151, 0.399, and 0.749). Hydrate dissociation conditions have been measured using an isochoric pressure search method in the 275.1–291.0 K temperature range and 0.67–19.07 MPa pressure range. The obtained experimental clathrate hydrate dissociation data have been compared with the predictions of two thermodynamic models, namely CSMGem and HWHYD, available in open literature. Finally, the thermodynamic promotion effects of TBAB in aqueous solutions are discussed in terms of hydrate dissociation pressures and temperatures and consequently the most favorable operating conditions are proposed.

1. Introduction

According to the Intergovernmental Panel on Climate Change (IPCC) special report on Carbon dioxide Capture and Storage (CCS) [1], the power plants activity constitutes more than 60% of carbon dioxide (CO_2) emissions, where nitrogen (N_2) and CO_2 are the most significant components. The majority of CO_2 emission sources have CO_2 concentrations of less than 15% [1]. However, a small portion of the fossil fuel-based industrial sources has CO_2 concentrations in excess of 95% [1]. Depending on process conditions (*e.g.* CO_2 concentration, pressure and fuel type), three conventional strategies have been established to capture CO_2 from industrial/flue gases, namely: post-combustion, pre-combustion; and oxy-fuel combustion. The first two approaches are considered economically feasible under specific conditions, while the third one is at demonstration phase [1]. Resulting from a concise literature review [2–9], the major benefits and drawbacks of these three main capture approaches are summarized in Table 1.

It is nowadays expected that new technologies are developed in order to decrease the costs of the CCS processes [1]. An alternative method for separating CO_2 from multi-component gas streams is through gas hydrate formation [10,11]. Gas hydrates (or clathrate hydrates) are crystalline solids ice-like, non stoichometric compounds of suitably sized small (guest) molecules and water (host) [12,13]. They can be formed under low temperatures and high pressures as a result of a physical combination. On a molecular scale, single guest molecules such as CO_2 and N_2 [14] are encaged by hydrogen-bonded water cavities [13].

Besides pressure, temperature, and composition of the gas mixture, the formation and dissociation of gas hydrates may be affected by the use of chemical additives with inhibition or promotion effect. The use of hydrate promoters has been proven to reduce the pressures required for hydrate stability and increase the gas hydrate equilibrium temperature and/or formation rate along with possible modification of the selectivity of hydrate cages for encaging various guest molecules in the water cages [15,16]. In recent years, considerable efforts have been made to investigate gas hydrate crystallization approach for separating a specific gas constituent from a multi-component gaseous mixture under favorable

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Table 1
Main features of post-combustion, pre-combustion and oxy-fuel combustion CO_2 capture approaches [2–9].

Capture approach	Separation task	Main method	Current application	Advantages	Drawbacks
Post-combustion	CO_2/N_2	Absorption (chemical solvents)	Separation of CO_2 from natural gas	Well established process Solvent can be recycled Degree of CO_2 purity >95% Non dependence on human operators minimizes labor costs Can be incorporated in existing power plants without significant modifications	High regeneration costs Degradation of solvents due to the presence of impurities and by-products Low CO_2 loading capacity Solvent can form corrosive solutions with flue gases. Lost solvent precipitates. Large equipment size
		Adsorption (solid sorbents)		Commercially available Sorbent can be reused Low concentrations of CO_2 yield an optimum performance	Sorbent susceptible to degradation Cannot handle easily large concentrations of CO_2 Adsorption time is not practical Low degree of CO_2 separation Poor selectivity of sorbents to CO_2 Operation costs higher than absorption processes
Pre-combustion	(Mainly) CO_2/H_2	Physical absorption *e.g.* Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA)	Production of hydrogen (mainly for fertilizer manufacture)	Requires less energy for regeneration than chemical absorption processes Less expensive than post-combustion capture	Requires a high partial pressure of CO_2 in the feed Capacity proportional to CO_2 partial pressure and temperature Low selectivity of solvent causes H_2 losses
		Membrane separation		Commercially available Require low maintenance Less energy intensive than PSA	Low degree of selectivity to CO_2
Oxy-fuel combustion	O_2/N_2	Cryogenic separation	Refinery of CO_2	Flue gas is mostly CO_2 and H_2O Water can be removed by condensation Separation of CO_2 is relatively inexpensive No need of control equipment for impurities Smaller size of equipment since only O_2 is supplied for combustion	Corrosion might be caused by SO_2 High cost of O_2 production Operation and capital costs similar to post-combustion processes

temperature and pressure conditions. The details of these studies can be found in a comprehensive review by Eslamimanesh et al. [16]. Hence, acetone, cyclopentane, surfactants, propylene oxide, 1,4 dioxane, tethahydrofuran (THF) or tetraalkyl ammonium salts are some of the chemicals that have been studied as gas hydrate promoters [15–17].

The formation of hydrates of tetra alkylammonium salts was, perhaps, first studied by Fowler et al. [18] in 1940 and further investigated by McMullan and Jeffrey in 1959 [19] and later by Dyadin and Udachin [20] in 1984. Tetra-n-butylammonium bromide (TBAB) is a quaternary ammonium salt that has been proposed as an environmental friendly hydrate promoter [21,22] for industrial/flue gas separation [21–28], storage [28,29] and transport [30,31] applications in the form of semi-clathrate hydrates. In TBAB semi-clathrates, the cations fulfill the void-filling role of the gases in the gas hydrates and the anions are hydrogen-bonded with the water molecules to form part of the clathrate cage structure [21–33]. TBAB forms different hydrate crystal structures depending on its concentration in aqueous solution [14,34,35].

Shimada et al. [22], found that TBAB hydrate crystals could be used to separate gas molecules which fit the empty dodecahedral cages and concluded that these empty cages function as a sieve for gas molecules [22]. Despite the current need for developing alternative methods for CO_2 capture and the potential application of TBAB semi-clathrate hydrates in the selective removal of CO_2 from industrial/flue gases, dissociation data available in the literature for $CO_2 + N_2 +$ TBAB semi-clathrate hydrates are scarce. Duc et al. [28] used a solution of 0.29 mol% of TBAB to decrease the equilibrium pressure of mixed ($CO_2 + N_2$) hydrate, with loadings of (0.155; 0.192; 0.215 and 0.234 mole fraction of CO_2). The effect of 0.293 mol% TBAB on CO_2 separation efficiency from CO_2 (16.60 mole%) + (83.40 mole%) N_2 binary mixtures by formation of semi-clathrate hydrates at 277.65 K and feed pressures ranging from 3.36 to 7.31 MPa was studied by Fan et al. [23]. Their results demonstrated that CO_2 could be remarkably enriched in the hydrate phase in the presence of TBAB even under lower feed pressure. Also in 2009, equilibrium formation pressures of CO_2 (0.159 mole fraction) + (0.841 mole fraction) N_2 + TBAB were reported by Lu et al. [36] at (0.05; 0.153; 0.348; 0.407 and 0.457) TBAB mass fraction in the temperature range of 278.05–287.85 K. Deschamps and Dalmazzone [37] measured hydrate dissociation temperature and pressure conditions for the formation of semi-clathrates from a CO_2 (0.249 mole fraction) + (0.751 mole fraction) N_2 gas mixture in the presence of 0.4 mass fraction TBAB in aqueous solution by differential scanning calorimetry technique. The effect of TBAB concentration on the incipient conditions for