A thermodynamic approach to selection of suitable hydrate formers for seawater desalination

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ARTICLE INFO

ABSTRACT

An integrated thermodynamic approach for selecting a suitable hydrate former for desalination prior to process design is presented. From amongst the various formers reported in literature, methane, carbon dioxide (CO_2), ethane, propane and iso-butane were chosen for this investigation. Simulation studies related to formation of hydrates in pure and saline water (2–8 wt% salt) for the 5 chosen formers have been conducted to predict phase equilibria along with gas solubility in the aqueous phase. A commercial software HydraFLASH was used for this purpose. In addition, the hydration number and phase change enthalpy associated with hydrate formation/dissociation has been calculated, the latter determined using the Clapeyron equation. Simulation results wherever appropriate were validated with experimental data and good agreement was observed. The implications of the thermodynamic data obtained on desalination process design have been discussed to arrive at a suitable choice of former. The results favor propane and ethane as preferred candidates for hydrate based desalination.

1. Introduction

The increasing demand of clean water for human consumption and industrial development has led to seawater desalination being explored as a potential water source in recent years. Amongst the several desalination process routes investigated, thermal evaporation or distillation and membrane based operations like Reverse Osmosis (RO) have been exploited at commercial scale [1,2]. However thermal operations inherently continue to suffer from issues of large energy demand and corrosion while RO faces challenges of relatively high operating pressure (~40–80 bar), retentate handling and are prone to problems of membrane fouling and scaling. While both thermal and membrane based processes have undergone developments to address the above issues, there is still a need to develop novel process technologies that can enable seawater desalination on a large scale with emphasis on further reducing energy demand, corrosion and fouling. In this context, clathrate based desalination offers a potential and an exciting alternative.

Gas clathrates are non-stoichiometric crystalline class of inclusion compounds in which molecules of one component, i.e. guest is enclosed within a crystal structure framework of host molecules of another component [3]. The guest molecule, normally referred to as clathrate former, for most practical purposes is a gas. When the host molecule is water, the structure is referred as gas hydrate. Depending upon the type of guest molecule, hydrates show three different crystal structures: structure I or sI ($5^{12} + 5^{12}6^2$), structure II or sII ($5^{12} + 5^{12}6^4$) and structure H or sH ($5^{12} + 4^35^66^4 + 5^{12}6^8$). Some of the common sI hydrate formers include methane, ethane and carbon dioxide (CO_2). Nitrogen, propane and iso-butane are amongst the sII hydrate formers. The number of moles of hydrated water per mole of encaged former gas is known as hydration number (n_w). Different formers hold different number of water molecules based on their structure and formation conditions. This feature of hydration makes them suitable for seawater desalination.

Over the years, several studies have been conducted to exploit the application of clathrates for seawater desalination [4–19]. One of the earliest applications of hydrate desalination was the propane former based Koppers process which was demonstrated at pilot scale [4]. Since then, there has been a strong emphasis on the use of halogenated hydrocarbon based CFC and HCFC refrigerants as hydrate formers [5–9]. Barduhn et al. [5], using methyl bromide, Freon 21 and Freon 31 as hydrate formers for demineralizing sea water, have shown that the economics of such a process depends on former properties like equilibrium pressure − temperature, enthalpy of hydrate formation/dissociation, solubility of former in water and hydrate stability. Hydrate formation using these refrigerants in aqueous solutions with and

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Nomenclature

Symbols

G_f	former gas		Q	quadruple point
$\Delta\bar{h}$	enthalpy of phase change per mole of former gas ($kJ\,mol^{-1}$)		T	thermodynamic temperature (K)
			$\bar{v}_g$	molar volume of former gas ($m^3\,mol^{-1}$)
$\Delta\bar{h}_w$	enthalpy of phase change per mole of water ($kJ\,mol^{-1}$)		$\bar{v}_{hydrate}$	molar volume of hydrate ($m^3\,mol^{-1}$)
H	hydrate		$\bar{v}_{pure\,water}$	molar volume of pure water ($m^3\,mol^{-1}$)
I	ice		$\bar{v}_{salt\,water}$	molar volume of salt water ($m^3\,mol^{-1}$)
L	liquid water		$\Delta\bar{v}$	molar volume change associated with hydrate formation/dissociation
N_A	Avogadro's number		V	former vapor/gas
n_w	hydration number		x_g	molar composition of gas
N_w	number of water molecules in hydrate structure		x_w	molar composition of water
P	absolute pressure (bar)			

Greek letters

α	lattice parameter

without NaCl at various concentrations indicated a thermodynamic inhibition effect due to the presence of the salt [10]. While refrigerants have potential to form hydrates and desalinate sea water, some of them pose serious environmental impact i.e. atmospheric ozone layer depletion and are no longer preferred. In addition, their solubility in the aqueous phase can limit water quality to certain end applications only.

An early patent [11] presented a process for saline water conversion to potable water utilizing ethane hydrate at 23 bar and 286.15 K. Another patented apparatus for methane hydrate desalination has been described for deployment in polluted and brackish water bodies at a depth of 100 to 10,000 m with application pressures ranging from 10 bar to 1000 bar [12]. A pressure vessel combined with co-flow injection technology to form methane and CO_2 hydrate at ~70 bar for removal of salt and soluble materials from "produced" water in oil and gas fields has also been patented [13]. More recently, a study associated with removal of dissolved salt ions, by exploiting methane and CO_2 as hydrate formers in the pressure range of 60–100 bar has found CO_2 to be a more suitable former than methane [14,15]. Babu et al. [16], in a lab scale study, have reported unusual behavior of propane as co-guest with CO_2 former enhancing hydrate formation kinetics in saline water using a porous medium like sand. Water recovery in the range of 60–80% was achieved in 1 h at 40–60 bar pressure. It is interesting to note that the operating pressures are in general above 50 bar when methane and CO_2 are used as formers which is comparable with pressures encountered in RO based systems. Han et al. [17] have investigated a novel Hydrate Induced Ice Desalination (HIID) process using CO_2 as former. Hydrate formation in the reactor was observed in a relatively lower pressure range of 25–30 bar at a temperature of 273.35 K. Rapid, but controlled release of gas pressure subsequently resulted in a temperature which facilitated formation of ice devoid of salt. Salt rejection with 3.5 wt% NaCl was about 67%.

Over the years, several theoretical studies have also been conducted to predict phase equilibria of hydrate systems using different formers like nitrogen, methane, CO_2, ethane, propane, iso-butane and hydrogen sulfide [20–24]. Predominantly an Equation of State (EoS) with an appropriate mixing rule in combination with the van der Waals and Platteeuw model is employed to predict equilibrium pressures and temperatures along with composition in the solid and aqueous phase. These studies were however restricted to hydrate formation in pure water for single and mixed formers. The effect of electrolytic salts (e.g., Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Cl^-, and SO_4^{2-}) on hydrate phase equilibria has also been studied by researchers [25–29]. This effect has been modeled using the Pitzer or Aasberg–Petersen model to account for water activity in presence of these electrolytes.

Other than hydrate phase equilibria, phase change enthalpy associated with hydrate formation/dissociation in pure water has been predicted using the Clausius–Clapeyron [30] and Clapeyron equation [31,32]. The Clapeyron equation takes into account the finite volume of

liquid and hydrate phases as against only the vapor phase consideration accounted for in the Clausius–Clapeyron equation. A method developed by D. Avlonitis [33] based on the statistical theory of solid solutions of van der Waals and Platteeuw [20] has also been adopted for this purpose. Amongst these approaches, the Clapeyron equation has proven to be simple and reliable. However, the effect of electrolytes on phase change enthalpy has not been reported till date.

It is evident that a large amount of segregated work seeking to establish the potential of primarily CFC/HFC based refrigerants, propane, methane and CO_2 hydrates for desalination has been reported till date in literature which can be further explored from an application point of view. However every gas hydrate forms at different pressure–temperature (*P–T*) conditions and hydrate forming agents have respective water solubility, enthalpy of phase change, and stability. While previous investigations emphasize on the feasibility of the hydrate based desalination process, the basis for selection of hydrate former for large scale application prior to the design stage has not been discussed adequately.

In the present study, an integrated approach to selection of a suitable hydrate former for desalination based on a detailed thermodynamic analysis inclusive of phase equilibria, hydration number, solubility and hydrate formation/dissociation enthalpies is presented. Based on this analysis, suitable formers have been proposed prima facie for the application of hydrate technology for desalination.

2. Materials and methods

While the potential of methane, propane and CO_2 as hydrate formers has been extensively researched and a few articles reported on ethane, there is very little reported on iso-butane as a former for desalination. In this context, these 5 gases were chosen for this study.

2.1. Hydrate phase equilibrium conditions

A built-in EoS which accounts for the non-ideality of components in combination with an appropriate mixing rule was used to model the gas and liquid phase. Amongst the various EoS models available, four have been primarily investigated over the years by researchers [21–24] to describe phase equilibria in gas hydrate systems namely, Cubic Plus Association (CPA), Saove–Redlich–Kwong (SRK), Peng–Robinson (PR) and Valderrama–Patel–Teja (VPT). Of these, the VPT model along with the Non-Density Dependent (NDD) mixing rule has been extensively used to describe non-ideality in gas and liquid phase. For all further purposes in this study, the VPT with NDD was used to predict hydrate equilibrium pressures in pure water in the temperature range of 260 K to 290 K. The hydrate phase was modeled using the solid solution theory of van der Waals and Platteeuw [20] which was also built into the software. The van der Waals and Platteeuw model accounts for the