



Experimental study and modeling of the kinetics of refrigerant hydrate formation



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ABSTRACT

The purpose of this study was to identify compatible hydrate forming-refrigerants suitable for air-conditioning systems. The main challenge in designing an air conditioning system which utilises refrigerant hydrates as a media for storage of cold energy is the rate of formation and dissociation of the refrigerant hydrates. Hence, in this experimental study the kinetics of hydrate formation of three refrigerant blends, viz. R407C, R410A and R507C have been investigated. The induction time for hydrate formation, apparent rate constant of the hydrate reaction, water to hydrate conversion during hydrate growth, storage capacity, and the rate of hydrate formation of these refrigerants at various pressures and temperatures have been obtained using a kinetic model. The effect of sodium dodecyl sulfate (SDS) on the hydrate nucleation rate was also investigated.

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1. Introduction

Air-conditioning has become an essential requirement in modern society to ensure a comfortable and consistent working and living environment; however the ever-growing application of this technology, especially in commercial buildings, creates a great imbalance between the demand and supply of electrical power during peak demand hours. These peak loads may require expensive generators to meet these high demand loads and results in expensive generating capacity that is under-utilised during off-peak demand periods. One solution to this problem is to have distributed cold storage technology which can be charged during the night and discharged during the day using little peak hour or high demand electricity. Hence, the strategy of demand side load management (DSLMM) by distributed cold storage systems has attracted a great deal of interest and various cold storage methods and materials have been proposed to date [1–8]. The typical storage materials are ice, water, and eutectic salt; however some of the deficiencies of such materials (e.g. low density of cold storage and low efficiency of heat exchanging) has forced researchers to

look for more efficient and practical storage materials. It was found that low pressure gas hydrates have great potential to be used as a storage material in cold storage applications due to their outstanding properties such as large cold storage capacity (high enthalpy of formation) and high cold storage efficiency (formation temperature above the freezing point of water) [1,4,5]. Low pressure refrigerant hydrates have tremendous prospects as cold storage materials in cold storage applications and numerous studies have been carried out on their formation/dissociation conditions so far [1,3,9–12]. However, in order to achieve a more practical and economical cold storage system the hydrate formation needs to be instantaneous. There are few studies which have considered the rate of the refrigerant hydrate formation in the open literature. A study undertaken by Mori and Mori [5] revealed the physical process of gas hydrate formation in a crystallizer (i.e. a cold storage tank) incorporated into an R12 vapour compression refrigerator loop. However, the Montreal Protocol eliminated the use of chlorofluorocarbons (CFC) refrigerants in the mid-1990s and the consideration of alternative refrigerants has since been established. The effect of some additives on the degree of sub-cooling before formation of the R134a hydrate was studied by Isobe and Mori [3]. They found that the degree of sub-cooling decreased with the addition of powdered alumina or zinc or the addition of surfactant to the water, while the addition of *Pseudomonas* fluorescence, a strain of ice-nucleating bacteria, showed no effect.

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The effect of an SDS solution as well as the metal rod on the kinetics of R141b hydrate formation was studied by Li *et al.* [13]. The amount of cold energy, growth rate, Hydrate Packed Factor (HPF) and overall heat transfer coefficient during the cold storage process were calculated and analyzed by Xie *et al.* [14] using different heat exchangers, sodium dodecyl sulfate (SDS) concentrations, hydration enhancement ways, inlet coolant temperatures, and flow rates. The cold storage and release process of the R134a hydrate in the presence of alcohol additives was studied by Wu and Wang [7]. The main challenge in the practical application of cold storage using gas hydrates is the slow formation rate of the gas hydrate. Hence, in this communication a different aspect of refrigerant hydrate formation has been studied and the kinetic behaviour of alternative refrigerants R410a, R407C, and R507C hydrates have been investigated. Induction time, storage capacity, water to hydrate conversion, and the apparent rate constant of hydrate formation have been measured for the aforementioned refrigerants and compared. The effect of sodium dodecyl sulfate on hydrate formation and growth rate has also been considered. Hydrate nucleation has been inferred according to the gas hydrate nucleation theory, and the hydrate growth has been analysed by using a (diffusion + reaction) kinetics model.

2. Experimental section

2.1. Materials

The details of the suppliers, the purities of the chemicals used in this study as well as their costs are reported in table 1. In an economical point of view R407 C has the lowest price comparing to the other refrigerants considered in this study and R507C has the highest price. The reported purities are as stated by the suppliers in their product certificates. Ultrapure Millipore Q water with an electrical conductivity of 18 M Ω cm obtained from UKZN laboratories was used in the experiments.

2.2. Apparatus

The main part of the experimental apparatus consists of a high pressure stainless steel equilibrium cell with an internal volume of approximately 40 cm³ which can withstand pressures up to 20 MPa. The contents of the cell are agitated using a mechanical stirrer placed at the top of the equilibrium cell which is connected to a stirrer motor. The temperature of the cell is controlled using a thermostatted bath with a claimed stability of ± 0.1 K. The temperature of the cell is measured using a Pt100 (platinum temperature probe) connected to the cell. The Pt100 was calibrated using a WIKA primary temperature probe which was connected to a WIKA CTH 6500 multimeter. The pressure of the cell is measured using a WIKA pressure transducer with an uncertainty of $\pm 0.05\%$ of full scale. The calculated overall expanded uncertainties in the

temperature and pressure measurements are ± 0.1 K and ± 0.005 MPa, respectively.

2.3. Procedure

At the beginning of each run, the equilibrium cell was cleaned and washed with deionized water. After initial evacuation of the cell, approximately 16 cm³ water was loaded into the cell which was then evacuated to 0.001 MPa for a period of at least 30 min. The cell was then immersed into the temperature controlled bath and the temperature of the cell was set to a desired temperature. After stabilization of the cell temperature, the cell was pressurized to a desired pressure (within the hydrate stability zone) by introduction of the refrigerant into the cell. After pressurizing the cell, the stirrer was turned on and set at a speed of 620 rpm for all measurements. As can be observed from figure 1, hydrate formation was confirmed by increasing of the cell temperature and decreasing of the cell pressure (due to the exothermic nature of gas hydrate reaction). The induction time is specified as the time over which the temperature remains at the defined value before the inception of a significant temperature change in the system. After initiation of hydrate formation inside the cell, the pressure decreases continuously until a steady state condition is reached, at which the pressure of the cell remains constant. In order to verifying the reproducibility of the induction times the experiments were conducted twice and the reproducibility of less than one minute obtained for the induction time. The Peng–Robinson equation of state (PR EoS) EoS modified by Stryjek and Vera (PRSV) [15] was employed to calculate the amount of gas consumed during hydrate formation.

3. Kinetic model of hydrate growth

It was assumed that hydrate nucleation and growth occur only in the liquid film at the gas–liquid interface. According to the hydrate growth kinetic model proposed by Englezos *et al.* [16,17], the rate of hydrate reaction ($r(t)$) can be expressed as:

$$r(t) = \frac{dn}{dt} = k_{app}(f - f_{eq}), \quad (1)$$

where n is the moles number, t represents the time, k_{app} stands for the rate constant of hydrate reaction, f is the fugacity of the refrigerant at instantaneous pressure and temperature; and f_{eq} is the equilibrium fugacity of the refrigerant at the equilibrium pressure ($P_{equib.}$) and initial temperature. More details concerning the calculation of the equilibrium pressure can be found in a complementary study [18]. In this study, the amount and rate of gas consumption, storage capacity of gas hydrate, water to hydrate conversion, and rate constant during formation of various refrigerant hydrates have been calculated.

TABLE 1
Purities and suppliers of the refrigerants studied.

Chemical	Formula	^a Purity	Unit price/US \$/kg	Supplier
Distilled water	^b H ₂ O			UKZN
SDS	C ₁₂ H ₂₅ NaO ₄ S	0.990	^d 1400	Sigma–Aldrich
R407C	^c 0.23CH ₂ F ₂ + 0.52CH ₂ FCF ₃ + 0.25CHF ₂ CF ₃	0.998	^e 6.7	Afrox
R507C	^c 0.5CH ₃ CF ₃ + 0.5CHF ₂ CF ₃	0.998	^e 30	Afrox
R410A	^c 0.5CH ₂ F ₂ + 0.5CHF ₂ CF ₃	0.998	^e 10	Afrox

^a Mole fraction as stated by supplier.

^b Ultrapure Millipore Q water with an electrical conductivity of 18 M Ω cm.

^c Mass fraction as stated by supplier.

^d Sigma–Aldrich company 11/08/2013.

^e As stated by Afrox company, valid in 09/08/2013.

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