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Experimental measurements and thermodynamic modeling of refrigerant hydrates dissociation conditions

Hamed Hashemi[a,b], Saeedeh Babaee[a,b], Amir H. Mohammadi[a,c,*], Paramespri Naidoo[a], Deresh Ramjugernath[a,*]

[a] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V, Avenue, Durban 4041, South Africa
[b] Department of Chemical Engineering, Buinzahra Branch, Islamic Azad University, Buinzahra, Iran
[c] Institut de Recherche en Génie Chimiqueet Pétrolier (IRGCP), Paris Cedex, France

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ABSTRACT

This study aims to investigate dissociation conditions of refrigerant hydrates both experimentally and theoretically. For this purpose, dissociation conditions of refrigerants R23, R134a, R125a, R22, R410A, R407C and R507C have been measured experimentally. A thermodynamic model that is able to predict refrigerant hydrates dissociation conditions in the various phase equilibrium regions has been proposed as well. Refrigerants modeled in this study include pure refrigerants: R11, R12, R13, R22, R23, R32, R134a, R141b, R143a, R125a, R152a, and mixed refrigerants: R11 + R12, R11 + R114, R12 + R114, R32 + R125a + R134a (R407C), R32 + R125a (R410A). For the modeling of the fluid and hydrate phases, the Peng-Robinson equation of state modified by Stryjek and Vera and the MHV2 G^E-EoS mixing rule along with the UNIFAC (original) activity coefficient and van der Waals–Platteeuw (vdW–P) models were employed. The results show good agreement between the experimental and predicted values.

1. Introduction

The high consumption of electrical energy by air-conditioning and refrigeration processes during peak usage periods, especially in summer times, as well as a need for almost instant cooling in motor vehicles have encouraged researchers to look for more economical and efficient air conditioning systems. Cold storage technology, in which cold energy is added to a storage medium and later removed for use at another time, is a promising solution to these problems. Generally an air conditioning system which utilizes cold storage technology is comprised of a storage medium, a cooling circulator (*e.g.*, chilled water, alcohol, refrigerant), a pump and a condenser. Due to the essential role of the storage media in cold storage technology, numerous studies have been carried out for the design of an effective storage tank. Conventional materials in cold storage applications, such as ice, eutectic salt, and water suffer from the disadvantages of low efficiency, low density of cold storage, and low efficiency of heat exchanging, respectively [1]. Continued research to find a better cold storage media has led to the consideration of gas hydrates [1–4]. Gas hydrates or clathrate hydrates are ice-like components which form with the guest molecule(s) and water. In the crystal structure of the hydrates, water molecules are bonded to each other through hydrogen bonding and result in the formation of cavities which can be filled with one or more guest molecules of the appropriate size and shape. Depending on the size and shape of the guest molecules hydrates can be classified into three distinguished structures I, II or H [5].

Most refrigerant hydrates are considered to be an ideal cold storage medium, especially suitable for air conditioning systems due to their outstanding properties, for example their large cold storage capacity (high enthalpy of formation) and high cold storage efficiency (formation temperature above water freezing point) [6]. A comprehensive review of cold storage materials and thermal energy storage can be found in literature [7,8]. Since the first utilization of gas hydrates as a medium for cold storage applications in 1982, when American scientists proposed using Freon hydrate as cool storage medium [2], many experimental studies have been carried out to date [1,3,9–16]. The hydrate formation conditions of R11, R12 and their mixtures have been measured by Carbajo [6] who found that the mixture of R11 + R12 at a specific composition may form hydrate at a pressure close to atmospheric pressure which is beneficial in the design of a cold storage tank [6]. Mori and

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* Corresponding authors at: Institut de Recherche en Génie Chimiqueet Pétrolier (IRGCP), Paris Cedex, France (Amir H. Mohammadi), Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V, Avenue, Durban, 4041, South Africa (D. Ramjugernath).

E-mail addresses: a.h.m@irgcp.fr, amir_h_mohammadi@yahoo.com (A.H. Mohammadi), ramjuger@ukzn.ac.za (D. Ramjugernath).

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Nomenclature

a, b	parameters of equation of state (EoS)
C_{jm}	Langmuir constant (equations (4) and (7))
f_w^H	fugacity of water in the hydrate phase (equation (1))
f_w^β	fugacity of water in the empty hydrate lattice (equation (2))
$f_w^{L/I}$	fugacity of pure water in liquid phase or ice (equation (2))
f_j	fugacity of the gas component j (equation (3))
g	Gibbs free energy (equations (17) and (19))
R	universal gas constant (equations (19) and (20))
R_k	UNIFAC volume parameter (equation (25))
Q_k	UNIFAC surface area parameter (equation (26))
z	mole fraction (equations (17)–(19))

Greek letters

$\Delta\mu_w^{\beta-H}$	difference between the chemical potential of water in the empty hydrate lattice and the hydrate phase (equation (3))
$\Delta\mu_w^{\beta-L/I}$	difference between the chemical potential of water in the empty hydrate lattice and the liquid phase or ice (equation (8))
$\Delta\mu_w^0$	reference chemical potential difference between water in the empty hydrate lattice and pure water in the ice phase at $T = 273.15$ K (equation (8))
$\Delta h_w^{\beta-L/I}$	molar enthalpy differences between an empty hydrate lattice and liquid water or ice (equation (8))
ΔC_{pw}	heat capacity difference between the empty hydrate lattice and the pure liquid water phase (equation (10))
$\Delta v_w^{\beta-L/I}$	volume differences between an empty hydrate lattice and liquid water or ice (equation (8))
$\bar{v}_m$	number of cavities of type m per water molecule in the unit hydrate cell (equation (3))
$w(r)$	spherically symmetric cell potential in the cavity (equation (4))
å	characteristic energy (equation (5))
σ	collision diameter (equation (6))
a	radius of spherical molecular core (equation (6))
α	attractive parameter of a cubic EoS (equation (20))
γ_i	activity coefficient of component i (equation (19))
θ_i	area function (equation (22))
Φ_i	segment function (equation (22))
v_{ki}	number of groups of kind k in molecule i (equation (25))
Γ_k	residual activity coefficient of group k in a solution (equations (27))

Mori [9] measured some experimental data using R12 as the refrigerant in cold storage connected to the refrigeration cycle. Although the CFC refrigerants such as R11 and R12 have been considered as an appropriate media for cold storage applications, these materials have been restricted by the Montreal Protocol due to their high ozone depletion potential (ODP). Hence, studies on gas hydrate formation/dissociation using CFC alternatives has been undertaken since the end of 1980s. Hydrate formation conditions as well as enthalpy of dissociation of some refrigerant alternatives, HFC-32, HFC-125, HFC-134 and their mixtures R410A and R407C have been reported by Akiya *et al.* [17].

Apart from the refrigerant hydrates capability of being decent media in cold storage applications, it has also been well established that refrigerant hydrates can be used for other chemical engineering applications such as desalination and purification of saline and waste water and in the food and pulp industry for producing fluid concentrates [18–23]. Hydrate dissociation data for R13, R23 and R152a have been measured by Kubota *et al.* for the design of a desalination process using sea water with the means of hydrates [24]. In this process the dissociation of the formed refrigerant hydrate produces refrigerant and pure water in which the released refrigerant is then recycled in the hydrate formation unit. The formation and dissociation characteristic of the hydrate of refrigerants, R11 (CCl3F) and CH3Br, in various aqueous solutions containing carbohydrates, proteins, or lipids as well as the concentration of apple, tomato and orange juices using these refrigerant hydrates can be found in literature [25,26].

Prior to the design of such hydrate-based processes, accurate equilibrium data are required. Consequently, in order to evaluate the experimental data, the development a theoretical model is inevitable.

Hence in this study, phase equilibria of some refrigerant hydrates including R22, R23, R134a, R125a, R410A, R407C and R507C have been measured experimentally. In the case of R507C, these data are new and for R410a and R407C only one set of data has been reported in literature to date. A comprehensive model which can predict the experimental hydrate dissociation data of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), fluorocarbons (FCs) and some of their mixtures is also presented. For this purpose a thermodynamic model based on the van der Waals–Platteeuw (vdW–P) solid solution theory [27] was developed.

It should be mentioned that although the CFC refrigerants are no longer being used due to their high ozone depletion potentials (ODP), it is however necessary to be aware of their hydrate dissociation conditions for hydrate capturing processes. Therefore, the modeling of CFC's has been investigated in this study.

The results obtained in this study may be used in further experimental hydrate measurements for the refrigerants and their mixtures and hydrate based processes which involves refrigerant hydrate formation.

2. Experimental section

2.1. Materials

The suppliers of the refrigerants used in this study, as well as the purities of the refrigerants are reported in table 1. The reported purities are as stated by the suppliers in their product certificates.

2.2. Apparatus

A schematic diagram of the experimental setup is shown in figure 1. The main part of the experimental apparatus is a high pressure stainless steel equilibrium cell with an internal volume of approximately 75 cm^3 which can withstand pressures up to 20 MPa. The contents of the cell are agitated using a magnetic stirrer bar magnetically coupled to a U-shaped magnet which is connected to a stirrer motor beneath the cell. The temperature of the cell is controlled using a thermostatted bath within an uncertainty 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 WIKA CTH 6500 multimeter. The pressure of the cell is measured using a WIKA pressure transducer with an uncertainty within ±0.05% of full scale. The calculated