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The role of thermal path on the accuracy of gas hydrate phase equilibrium data using isochoric method

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ABSTRACT

The aim of this paper is to investigate the role of thermal path on the accuracy of gas hydrate phase equilibrium data using isochoric method. In this regard, methane hydrate equilibrium conditions have been typically determined using different heating paths – continuous and stepwise. The step-heating path, with proper size and duration of temperature increment, provided the most accurate data of methane hydrate phase equilibrium conditions compared with other experimental data available in literature. We have concluded that equilibrium step-heating path had the potential for determining reliable hydrate phase diagrams, irrespective of the present components in the system. Generally, the sufficient time given to each isothermal step is based on approaching a constant number of moles of gas phase through partial hydrate dissociation whereas the size of temperature increment is limited by the amount of gas encaged in hydrate cages.

Moreover, the advantage of isochoric method for pure gas systems in utilizing a section of hydrate phase diagram instead of the distinctive condition, at which the last piece of hydrate disappears, is confirmed. Finally, the possibility of obtaining hydrate phase diagram of pure gas systems at arbitrary pressures was examined by purging the system before hydrate dissociation process.

1. Introduction

Gas hydrates are solid non-stoichiometric compounds formed from the contact of water with gas molecules above the water freezing point at relatively high-pressures. The crystalline structure is stabilized with respect to the non-covalent interactions between the gas and the water molecules. Three known structures (sI, sII and sH) are distinguished for hydrate crystals depending on the nature and size of the guest molecules [1–3].

Over a century after the discovery of gas hydrate, it came into researchers' interest with respect to the cause of natural gas pipeline blockage [3,4]. In the oil and natural gas industry, knowledge of hydrate equilibrium phase diagrams play the primary role in gas hydrate flow assurance, i.e. controlling and preventing hydrate formation. It is not allowed that the operating conditions of pipeline exceed the limits of gas hydrate thermodynamic stability zone and/or be shifted to lower temperatures using thermodynamic inhibitors [2–4]. Three static methods are mentioned in literature to obtain hydrate equilibrium phase diagram. Isothermal pressure-search and isobaric temperature-search methods are based on visual observation of hydrate dissociation using a transparent windowed vessel [2,3] and details of the related procedures and apparatus can be found elsewhere [3,5–8]. The application of visual methods has been limited to conditions with relatively low pressure and temperatures above the freezing point of water because of the similar features of hydrate and ice crystals [9].

Isochoric method, used for the determination of hydrate equilibrium phase diagrams, is based on a cooling/heating cycle at constant volume. This method can be also coupled with visual observation [10–13]. Hydrate formation is initiated under adequate sub-cooling and crystal growth is detected from a sharp pressure drop since the temperature is kept constant at constant volume. After hydrate completion, hydrate dissociates through heating path [1,14]. In the corresponding pressure–temperature diagram, intersection of cooling and heating path is considered as the thermodynamic equilibrium point. It is believed that heating curve passes through Lw-H-V equilibrium condition if hydrate is dissociated in equilibrium manner [14].

In this regard, some researchers have focused on investigating the accuracy of experimental equilibrium data obtained using different heating path. Schroeter et al. reported that continuous heating or cooling path with a rate of 0.1 K/h insure the hydrate

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Nomenclature

ΔT	difference between experimental hydrate equilibrium temperature and the one predicted by HWHYD model (K)
AAD	average absolute deviation (K)
Lw-H-V	three phase diagram of aqueous liquid–hydrate–vapor
N	number of experimental hydrate equilibrium data
n_0	initial moles of gas phase at each isothermal step (mol)
n_{equi}	the mole of gas phase corresponding to the equilibrium pressure of methane hydrate reported in literature at each isothermal step (mol)
n_g	number of moles of gas phase (mol)
$n_{\max}$	maximum moles of gas phase at each isothermal step (mol)
P	pressure of the vessel (MPa)
R	gas constant (m^3 MPa/mol/K)
T	temperature of the vessel (K)
t	time (h)
T_{exp}	experimental hydrate equilibrium temperature (K)
T_{HWHYD}	hydrate equilibrium temperature predicted by HWHYD model (K)
V	volume of the vessel (m^3)
z	compressibility factor of gas phase

Subscripts

0	initial condition
equi	equilibrium condition
exp	experimental
g	gas phase
HWHYD	predicted by HWHYD model
max	final condition

Greek letters

Δ	difference

equilibrium dissociation and the reliability of the gas hydrate equilibrium conditions for the three-component system of H_2S, Methane and propane [9]. However, it is possible to decrease the long time expended for each experiment because of the low heating rate. For instance, Nixdorf and Oellrich applied a two-part continuous heating path in determining the equilibrium conditions for some pure gases and mixtures. They suggested that the former part with a fast heating of 10 K/h was allocated to expansion of gas phase and the latter one with slow heating rate of 0.2 K/h was resulted in equilibrium hydrate dissociation [15].

Tohidi et al. used another heating pattern for methane hydrate dissociation. Using stepwise heating, they reported that consuming more time for each temperature step results in more accurate hydrate equilibrium point [14]. They also determined hydrate equilibrium conditions for natural gas by stepwise heating. Considering temperature step of 0.1 K, they reported less scattered and more accurate hydrate equilibrium point for slow heating duration of 6 h compared with fast heating duration of 10 min. In addition, they suggested that three equilibrium points obtained by stepwise heating is sufficient for obtaining the intersection of heating and cooling line and as a result, the time and the expense for each experiment is reduced [16]. Step-heating path was used for obtaining hydrate equilibrium data of pure methane, carbon dioxide, carbon monoxide [17], even in the presence of salts together with organic inhibitor [18]. In particular, step-heating path was recently used for compositional analysis of two-component systems such as $CO_2 + H_2$, $CO_2 + N_2$, and $CO_2 + CH_4$ along with hydrate dissociation condition measurements [10–12].

In this study, a generalized isochoric method was presented for obtaining reliable gas hydrate phase diagrams. For this purpose, methane hydrate equilibrium conditions were typically determined using different heating path in order to dissociate the hydrate phase. Two different thermal paths including continuous and stepwise heating were used. The reliability of heating paths was evaluated by comparing the accuracy of experimental equilibrium condition with the data given in the literature.

Moreover, the advantage of isochoric method for pure gas systems in utilizing a section of hydrate phase diagram instead of the distinctive condition at which the last piece of hydrate is disappeared was discussed. Finally, the possibility of obtaining hydrate phase diagram of pure gas systems at arbitrary pressures was examined by purging the system before hydrate dissociation process.

2. Experimental

2.1. Materials

Methane with a purity of 99.99% was purchased from Roham Gas Iranian Company. Deionized water (Barstead Nano Pure D4742; E.R. = 18 MΩ) was used.

2.2. Apparatus

Fig. 1 shows the scheme of the apparatus used for the determination of hydrate equilibrium phase diagrams. High pressure vessel (Parr Instruments, HC. 276) was 450 cm^3 and the safety valve was calibrated to release for pressure greater than 15 MPa. In order to set the temperature, the vessel was immersed in the bath of a programmable cooling thermostat (Lauda RP 855 C) with an accuracy of ±0.01 K. Pressure and temperature of the vessel were measured using a sensitive 4–20 mA pressure transducer (with a precision of ±0.3%) and a Pt100 thermometer (with a precision of ±0.1 K), respectively. According to the confidence interval of 95% under Gaussian probability distribution [19,20], the expanded uncertainties in the reported temperatures and pressures are ±0.2 K and ±0.6% MPa, respectively.

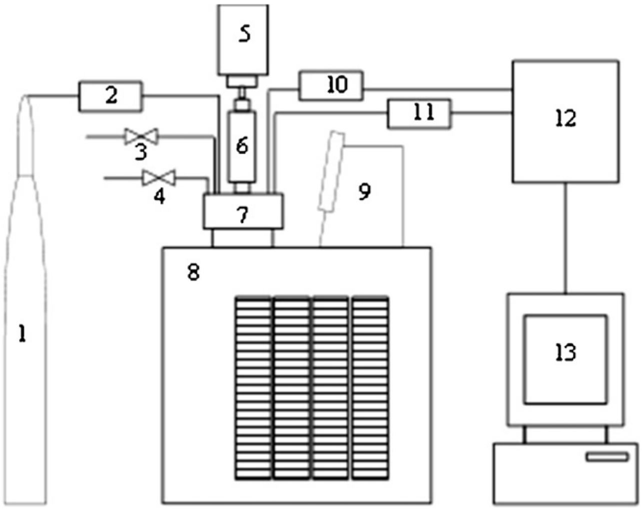

Fig. 1. Experimental apparatus: 1 – gas cylinder, 2 – pressure regulator, 3 – safty valve, 4 – sampling valve, 5 – electrical motor, 6 – magnetic drive, 7 – high pressure vessel, 8 – bath circulator, 9 – electronic temperature controller, 10 – pressure transducer, 11 – thermometer, 12 – data logger, and 13 – PC.