J. Chem. Thermodynamics 87 (2015) 122–128

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Experimental measurement and thermodynamic modelling of phase equilibria of semi-clathrate hydrates of (CO_2 + tetra-n-butyl-ammonium bromide) aqueous solution

Hesam Najibi [a,*], Kamalodin Momeni [a], Mohammad T. Sadeghi [b], Amir H. Mohammadi [c,d]

[a] Faculty of Petroleum Engineering, Petroleum University of Technology (PUT), Ahwaz, Iran
[b] Department of Chemical Engineering, Iran University of Science and Technology (IUST), Tehran, Iran
[c] Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France
[d] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

ARTICLE INFO

Article history:
Received 25 October 2014
Received in revised form 17 March 2015
Accepted 25 March 2015
Available online 2 April 2015

Keywords:
Gas hydrate
Semi-clathrate hydrate
TBAB
Carbon dioxide
Thermodynamic model

ABSTRACT

Comprehensive studies on semi-clathrate hydrates phase equilibria are still required to better understand characteristics of this type of clathrates. In this communication, new experimental data on the dissociation conditions of semi-clathrate hydrates of {carbon dioxide + tetra-n-butyl-ammonium bromide (TBAB)} aqueous solution are first reported in a wide range of TBAB concentrations and at different pressures and temperatures. A thermodynamic model is then proposed to predict the dissociation conditions of the semi-clathrate hydrates for the latter system. The (hydrate + TBAB) aqueous solution ($H + L_w$) phase equilibrium prediction is considered based on Gibbs free energy minimization approach. A modified van der Waals–Platteeuw solid solution theory developed based on the ($H + L_w$) equilibrium information is employed to predict the dissociation conditions of semi-clathrate hydrates of carbon dioxide + TBAB. The properties of the aqueous solution are estimated using the AMSA-NRTL electrolyte model (considering the association and hydration of ions). The Peng–Robinson equation of state is used for estimating the gas/vapour phase properties. Results show that the proposed model satisfactorily predicts the experimental values with an average absolute relative deviation of approximately 13%.

1. Introduction

Gas hydrates or clathrate hydrates are crystalline compounds formed by trapping the small size molecules (CO_2, CH_4, *etc.*) in the cage like lattice made of water molecules under low temperatures and elevated pressures [1]. Different crystalline structures for these lattices have been identified with the common known as structure I, structure II and structure H [1,2]. Each structure stabilizes at specified conditions of temperature and pressure mostly depending on the size of guest molecule [1]. Hydrate formation can cause pipeline blockage in oil and gas industry, leading to serious economical and safety damages [1–3]. Hydrates are interesting for researchers for their probable applications in different technologies such as gas separation, air conditioning, water desalination, natural gas storage and transportation and separation of greenhouse gases from atmosphere [1–7].

Carbon dioxide emission from fossil fuels combustion has drastically increased in last decades [7–9]. Carbon dioxide has a strong greenhouse effect and is the major responsible for climate change due to the presence of unpleasant gases in the atmosphere [7–11]. To separate carbon dioxide from flue and industrial gases, different technologies (Membrane, Alkanolamine Aqueous Solution, Cryogenic, Adoption, *etc.* based technologies) have been proposed so far [3,10,12–14]. A new technology that has been proposed recently for the separation of some gases is based on hydrate formation [3,7,15]. The hydrate of different gases stabilizes at different equilibrium conditions, therefore, the hydrate phase can trap specified gas while the concentration of other gases will increase in the gas phase [16]. The trapped gas in the hydrate phase can be released by depressurization or heating [3]. The major challenge facing this technique is the harsh condition required for hydrate formation (high pressure and low temperature) [1]. To ease the hydrate formation conditions, some materials known as "hydrate promoters" are normally added to the aqueous solution to improve the operational conditions and/or concurrently to alter the selectivity of the hydrogen-bonded water lattice for trapping the

---

* Corresponding author. Tel./fax: +98 61 35551754.
E-mail addresses: hesamnajibi60@gmail.com, najibi@put.ac.ir (H. Najibi).

http://dx.doi.org/10.1016/j.jct.2015.03.024
0021-9614/

molecules of interest (like CO_2 molecules) [17–20]. Several types of promoters have been used to change the operating conditions of hydrate formation of structures sI, sII or sH. One of them is tetra-n-butyl-ammonium bromide (TBAB) which forms semi-clathrate hydrate even at atmospheric pressure [21–27]. In the semi-clathrate hydrates produced in the presence of TBAB, some part of the hydrogen-bonded water lattice is broken and the anionic part of the hydrate former (Br^-) is confined in the network [21–27]. This will improve the gas trapping capacity of the cage and these hydrates will stabilize at moderate conditions of pressure and temperature [3,15,23,28–31]. Phase equilibrium of semi-clathrate hydrates is more complex than clathrate hydrates and requires more investigation [32]. The experimental data and theoretical models available to understand the phase equilibria of these compounds are still limited [15,28,31,33–41].

In this work, some experimental values for the phase equilibria of semi-clathrate hydrates of {carbon dioxide + tetra-n-butyl-ammonium bromide (TBAB)} aqueous solution have been measured in a wide range of salt concentrations and different pressures and temperatures. A thermodynamic model is proposed to predict the dissociation conditions of the semi-clathrate hydrates for this system. The (hydrate + TBAB) aqueous solution ($H + L_w$) phase equilibrium model is based on Gibbs free energy minimization. The van der Waals–Platteeuw (vdW–P) solid solution theory is modified to predict the dissociation conditions of semi-clathrate hydrates of carbon dioxide in the presence of TBAB. The properties of aqueous phase are estimated using the AMSA-NRTL electrolyte model and the Peng–Robinson equation of state (PR-EoS) is employed for calculation of the gas/vapour phase properties.

2. Experimental

2.1. Chemicals

Table 1 contains the values of the mole fraction purities and names suppliers of chemicals used in the experiments. The solutions were prepared by gravimetric method, using a digital balance with the accuracy of ±0.0001 g.

2.2. Apparatus

The measurements in this work were performed using the experimental apparatus shown schematically in figure 1. The equilibrium cell is made of stainless steel 316 with inner volume of approximately 100 cm^3 and maximum working pressure of 40 MPa. The cell is equipped with a 4 blade, variable speed magnetic stirrer. The cell temperature is controlled within 0.1 K using a bath (AMAR, HCB-324) by circulating coolant through a jacket surrounding it. The temperature of the cell is measured with a platinum resistance thermometer (Pt100) calibrated by ERDA research institute. The accuracy for temperature measurement is 0.1 K. The pressure is measured by means of a pressure transducer (WIKA instrument) with accuracy better than 0.01 MPa. The calibration of the pressure transducer is checked regularly using an accurate digital pressure gage (Ashcroft, 1070299) with an accuracy of 0.001 MPa.

TABLE 1
Provenance and mole fraction purity of chemicals used.[a]

Chemical	Supplier	Mole fraction purity
Carbon dioxide	Persian gas	0.99995
TBAB	Merck	⩾0.99

[a] Deionised water was used in all experiments.

2.3. Experimental procedure

In this work, semi-clathrate hydrate dissociation conditions were measured using a stepwise heating method [42]. For each run, approximately 25% (by volume) of the cell was filled with aqueous solution and then it was evacuated for four times to a vacuum level of 10^{-2} mbar and purged by CO_2. The cell was then pressurized to the desired level by introducing CO_2 and the stirrer was turned on. The cell temperature was decreased slowly to form the semi-clathrate hydrate of the (CO_2 + TBAB) aqueous solution. The lowest temperature was carefully determined to be higher than the semi-clathrate hydrate formation of pure TBAB ($H + L_w$ equilibrium). The cell temperature was then increased with a rate of $0.12\ K \cdot h^{-1}$ and it was kept constant until all the hydrates dissociated. When the slope of the (pressure + temperature) diagram changed suddenly, the hydrate dissociation point was determined [42–45]. It should be mentioned that the detailed method for estimating the standard uncertainty is given by *National Institute of Standards and Technology – NIST* [46] and *Bureau International des Poids et Mesures* [47]. Based on these methods, the maximum combined standard uncertainties (u_c) for the temperatures and pressures measured in this work are approximately $u_c(T) = 0.2$ K and $u_c(P) = 0.05$ MPa, respectively.

3. Thermodynamic model

The detail description of the model is presented as follows:

3.1. ($H + L_w$) phase equilibrium

The ($H + L_w$) phase equilibrium can be modelled by the Gibbs free energy minimization approach as described in ref [56]. The overall equation that describes this phase equilibrium is as follows:

$$\frac{\Delta g_{dis}(T,P)}{RT} = \frac{\Delta g^0(T_0,P_0)}{RT} + \frac{\Delta h^0(T_0,P_0)}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) - \frac{\Delta c_p^0(T_0)}{R}\left(\frac{T_0}{T}-1\right) + \frac{\Delta c_p^0(T_0)}{R}\ln\left(\frac{T_0}{T}\right) + \frac{\Delta \upsilon^0(P_0)}{RT}(P-P_0) + \ln(K_{ov}^{P_0}) = 0. \qquad (1)$$

The detailed description of different parameters in this equation is presented by Paricaud in reference [39]. In this equation, is the Gibbs free energy function at the reference condition including congruent melting temperature (T_0), atmospheric pressure ($P_0 = 0.101325$ MPa) and stoichiometric composition of the hydrate phase, Δh^0 is the molar enthalpy that can be experimentally determined [24,26], Δc_p^0 is the molar heat capacity that is set to zero to reduce the adjustable parameters, $\Delta \upsilon^0$ is the molar volume which is obtained by the Gibbs–Helmholtz equation at P_0 [48] and the attempt in this work is to find a suitable procedure for calculation the overall equilibrium constant at P_0 ($K_{ov}^{P_0}$).

TBAB forms a semi-clathrate hydrate crystal with υ_W water molecules per molecule of salt in aqueous solution. The following equilibrium reaction can be written for dissociation of this hydrate:

$$C_{\upsilon_C}A_{\upsilon_A} \cdot \upsilon_W H_2O(H) \overset{K_1}{\leftrightarrow} \upsilon_C C_{h_C}^{z_+}(aq) + \upsilon_A A_{h_A}^{|z|_-}(aq) + (\upsilon_W - h_C - h_A)H_2O(L_W), \qquad (2)$$

where C and A denote the cations and anions present in the salt with z_+ and $|z|_-$ charges, respectively and C_{h_C} and A_{h_A} are hydrated cation and anion in aqueous solution with h_C and h_A hydration number. Furthermore, the association reaction between the ionic