ARTICLE IN PRESS

J. Chem. Thermodynamics xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

A short note on modelling the three-phase equilibrium conditions of TBAB semi-clathrates formed in the presence of gas mixtures containing CO_2

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ARTICLE INFO

Article history:
Received 29 May 2017
Received in revised form 8 August 2017
Accepted 30 August 2017
Available online xxxx

Keywords:
Semi-clathrates
Tetra-n-butyl ammonium bromide
Tetra-n-butyl ammonium chloride
Phase equilibria

ABSTRACT

The model of Paricaud (2011) has previously been shown to be able to accurately correlate the three-phase equilibrium conditions of TBAB semi-clathrates in the presence of pure CO_2. While the model of Paricaud (2011) was derived in a manner that was expected to make it relatively straight forward correlating the three-phase equilibrium conditions of semi-clathrates in the presence of mixed gases this capability has not, at the time of writing, been tested. In the present work, the model of Paricaud (2011), along with the modification of Garcia et al. (2016), is examined for its ability to correlate the three-phase equilibrium conditions of TBAB semi-clathrates formed in the presence of binary mixtures of ($CO_2 + N_2$), ($CO_2 + H_2$), ($CO_2 + CH_4$), and (CO_2 + CO) and in the presence of a ternary mixture of ($CO_2 + H_2$+CO). The computations were carried out at temperatures between (281 and 293) K, at pressures between (2.0 and 6.6) MPa and in aqueous TBAB solutions of w_{TBAB} = (0.05, 0.10, and 0.20). The average absolute relative deviation of the correlations ranged from 3.7%, for TBAB semi-clathrates formed in the presence of an equimolar mixture of ($CO_2 + N_2$), to 7.1%, for TBAB semi-clathrates formed in the presence of a ternary gas mixture of ($CO_2 + H_2$+CO).

1. Introduction

Semi-clathrates are crystalline inclusion compounds that form when water and certain quaternary ammonium salts, such as Tetra-n-Butyl Ammonium Bromide (TBAB) are contacted at reduced temperatures [3,4]. As is apparent from their name, semi-clathrates share many commonalities with the more well-known clathrate hydrates, which are also known as gas hydrates. Both clathrate hydrates and semi-clathrates are comprised of a frame work of water molecules, which are capable of trapping large volumes of small gas molecules inside of a relatively small solid phase volume. However, unlike gas hydrates, semi-clathrates also incorporate the anion and cation of a salt into their molecular framework of water molecules; this allows semi-clathrates to form at much milder conditions than clathrate hydartes. Semi-clathrates can also form without the presence of a guest molecule [5,6].

Due their ability to trap large amounts of gas at relatively mild conditions, there has been much interest in exploring the possibility of using semi-clathrates as a medium for gas storage and gas separation [7–16]. This interest has spurred a healthy number of experimental studies related to the thermodynamics of semi-clathrate formation [5–7,15,17–37] as well as a handful of studies related to the kinetics of semi-clathrate formation [11,38,39].

In addition to the aforementioned experimental studies, several research groups have devoted attention towards correlating/predicting the three-phase equilibrium conditions for semi-clathrate formation. At the time of writing, all of the computational work related to semi-clathrate thermodynamics has been based on either the work of Eslamimanesh et al. [8] or Paricaud [1]. The only exception has been the work of Mohammadi et al. [40], who used estimated semi-clathrate formation conditions using a feed-forward neural network.

The model of Eslamimanesh et al. [8] has been the starting point for several subsequent thermodynamic modelling efforts [41,42]. While this model is relatively straightforward to implement it suffers from having a large number of adjustable parameters as well as from using an empirical correlation for the vapour pressure of TBAB which does not seem to have any physical meaning. Because of these limitations, it is doubtful whether the model of Eslamimanesh et al. [8] could be applied to correlating the equilibrium conditions for semi-clathrates formed in the presence of gas mixtures, without introducing any additional adjustable parameters.

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http://dx.doi.org/10.1016/j.jct.2017.08.040
0021-9614/© 2017 Elsevier Ltd.

Please cite this article in press as: N. Michel, M.A. Clarke, J. Chem. Thermodyn. (2017), http://dx.doi.org/10.1016/j.jct.2017.08.040

Unlike Eslamimanesh et al. [8], Paricaud [1] modelled the formation of semi-clathrates as a reaction equilibrium problem. In this approach, minimizing the Gibbs free energy of the reaction leads to a model that can be used to determine two-phase (liquid/-solid semi-clathrate) and three-phase equilibrium (vapour/liquid/-solid semi-clathrate) conditions. In the original work of Paricaud [1], the van der Waals and Platteeuw model [43] was used to describe the chemical potential of the solid phase and the Statistical Associating Fluid Theory (SAFT) with variable range for electrolytes [44] was used for modelling the fluid phases. Additionally, Paricaud [1] used the square well potential in order to compute the Langmuir constants. Paricaud [1] showed that not only was his model capable of accurately correlating the three-phase equilibrium conditions of TBAB semi-clathrates formed in the presence of CO_2, it was also able to correlate the two-phase equilibrium conditions of TBAB semi-clathrates in the absence of a gas. At the time of writing, the model of Eslamimanesh et al. [8] has not been shown to be capable of correlating the two-phase equilibrium conditions for TBAB semi-clathrates in the absence of any gases.

To date, the model of Paricaud [1] has only been incorporated into the modelling work of a handful of researchers [2,45,46] all of whom have used the model of Paricaud [1], or a minor variation, for correlating the equilibrium conditions of semi-clathrates in the presence of pure gases. In particular the work of Garcia et al. [2], which was itself a modification to the original model of Paricaud [1], is the foundation for the modelling effort that makes up the present manuscript. From hereafter the model of Paricaud [1] with the modifications of Garcia et al. [2] will be referred to as the model of Garcia et al. [2], for brevity sake.

The model of Garcia et al. [2] made two significant modifications to the original work of Paricaud [1]. These modifications were done with the intention of making the model accessible to those who are familiar with traditional gas hydrate equilibrium calculations but who are not thermodynamicists, *per se*. First, the electrolyte version of the PSRK equation of state was used for describing the fluid phases, instead of the SAFT equation of state. The electrolyte version of the PSRK equation of state [47] is a variation on the well-known SRK equation of state in which free energy mixing rules are employed. The PSRK equation of state, uses the LIFAC activity coefficient model [48] inside the free energy mixing rules in order to correlate the thermodynamic properties of electrolyte solutions and other non-ideal solutions. Second, the Kihara Potential function, which is commonly used for gas hydrate thermodynamic calculations, was used to compute the Langmuir constants instead of the square well potential. Garcia et al. [2] used their model to correlate the equilibrium conditions of TBAB and TBAC semi-clathrates formed in the presence of pure CO_2, CH_4, H_2, N_2, Ar and Xe.

In the present work, the model of Garcia et al. [2] is used to correlate the equilibrium conditions of TBAB semi-clathrates formed in the presence of binary and ternary gas mixtures containing CO_2. The effects of the gas phase composition are introduced by way of the mixing rules in the equation of state. For the components that were examined in the previous work, no additional parameters were required. The only parameters that were needed in the present study were the pure component parameters for CO, as this gas was not included in the database used by Garcia et al. [2].

2. Theory

2.1. The model of Paricaud

As noted in the introduction, the model of Garcia et al. [2] is a variation of the model of Paricaud [1] for describing the solid semi-clathrate phase. The derivation of the relevant equations will not be reproduced in detail in the present manuscript; interested readers can consult the cited works [1,2,47,48]. It should be noted, however, that the solid phase model used by Garica et al. [2] is the same as that of Paricaud [1].

The original model of Paricaud [1] was based upon the concept of reaction equilibrium and it was presented in two sequential steps: First, Paricaud's model [1] for solid-liquid equilibria is used in order to regress enthalpy and volume parameters for semi-clathrates formed in the absence of gases. This leads to the following expression, which describes the equilibrium condition between liquid electrolyte solution (TBAB) and a solid semi-clathrate, in the absence of any gases:

$$\frac{\Delta_{dis}G^0(T_0)}{RT_0}+\frac{\Delta_{dis}H^0(T_0)}{RT}\left(1-\frac{T}{T_0}\right)+\frac{\Delta_{dis}C_p^0(T)}{R}\left(1+\ln\left(\frac{T_0}{T}\right)-\frac{T_0}{T}\right)$$
$$+\frac{\Delta_{dis}V^0(T)}{RT}(P-P^0)+v_w\ln\left(x_w^L\gamma_w^L\right)+v_c\ln\left(x_c^L\gamma_c^L\right)+v_a\ln\left(x_a^L\gamma_a^L\right)=0 \quad (1)$$

In the above equation, $\Delta_{dis}G^0(T)$ is the standard Gibbs energy of dissociation, $\Delta_{dis}H^0(T)$ is the change in enthalpy accompanying the dissociation reaction of the semi-clathrate, $\Delta_{dis}C_p^0(T)$ is the change in heat capacity accompanying the dissociation reaction of the semi-clathrate, R is the Universal gas constant, T is the equilibrium temperature for semi-clathrate formation, P is the equilibrium pressure for semi-clathrate formation, the subscript o refers to the reference conditions, v_c is the stoichiometric coefficient of the cation, v_a is the stoichiometric coefficient of the anion, v_w is the stoichiometric coefficient of water γ_c^L is the activity coefficient of the cation in solution, γ_a^L is the activity coefficient of the anion in solution and γ_w^L is the activity coefficient of the water in the liquid solution. In the work of both Paricaud [1] as well as Garcia et al. [2], the term $\Delta_{dis}C_p^0(T)$ is set to zero because it was not believed to be significant over the temperature range where semi-clathrates form.

Subsequently, Paricaud [1] used the enthalpy and the volume parameters obtained for TBAB semi-clathrates in the absence of gases are used along with a modified form of the model of van der Waals and Platteeuw [43] in order to determine the equilibrium conditions for TBAB semi-clathrates in the presence of gases. The resulting equilibrium expression that needs to be solved for temperature is:

$$\frac{\Delta_{dis}G^0(T)}{RT}=\frac{\Delta_{dis}G^0(T_0)}{RT_0}+\frac{\Delta_{dis}H^0(T_0)}{RT}\left(1-\frac{T}{T_0}\right)+\frac{\Delta_{dis}V^0(T_0,P^0)}{RT}(P-P^0)$$
$$+v_w\ln(x_w^L\gamma_w^L)+v_c\ln(x_c^L\gamma_c^L)+v_a\ln(x_a^L\gamma_a^L)$$
$$-\sum_{i=1}^{N_{cav}}n_i\ln\left(1-\sum_{j=1}^{N_{gas}}Y_{ij}\right)=0 \quad (2)$$

In the original model of Paricaud [1], activity coefficients and fugacity coefficients were computed from the SAFT equation of state [44]. However, Garcia et al. [2] instead used the electrolyte version of the PSRK equation of state [47], along with the LIFAC activity coefficient model [48], to compute the fugacity coefficients and the activity coefficients that are needed in Eq. (2). The other difference between the original work of Paricaud [1] and the model of Garcia et al. [2] is that the latter used the Kihara Potential function, rather than the square well potential function, when computing the Langmuir constant; the Langmuir constant is subsequently used to compute Y_{ij} [49]. In addition to including the Langmuir constant, the term Y_{ij} is also an implicit function of the gas phase composition, which Garcia et al. [2] accounted for via the PSRK equation of state [47].