Thermodynamic modeling of hydrate dissociation conditions for refrigerants R-134a, R-141b and R-152a

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ABSTRACT

In this communication, a general model is presented for estimating hydrate dissociation conditions for refrigerants R-134a, R-141b and R-152a which employs the cubic plus association equation of state (CPA EoS) for modeling the fluid phases and van der Waals —Platteeuw statistical model for the hydrate phase. The Kihara potential parameters for the latter refrigerants are estimated by employing an implicit optimization scheme using minimization of the chemical potential difference of water in the hydrate and in the liquid phase. The minimization was performed by applying genetic algorithm. Using this model, the agreement between the experimental data and the model results is found acceptable.

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Modélisation thermodynamique des conditions dans lesquelles la dissociation des hydrates a lieu dans les cas des frigorigènes R-134a, R-141-b et R-152a

1.   Introduction

Gas hydrates (or clathrate hydrates) are ice-like crystalline compounds in which small molecules are entrapped in a cage of water molecules under high pressure and low temperature conditions (Sloan, 1990). Light hydrocarbons such as natural gas components and some refrigerants can form hydrate when come into contact with water under certain conditions of temperature and pressure. Hydrates consist of three main structures namely structure I (sI), sII and sH, respectively (Sloan, 1990).

Gas hydrate appears like ice, but they may form at temperatures well above the ice −point. Since gas hydrate dissociation is dramatically endothermic, it could be used in cool storage and air conditioning applications (Tomlinson et al., 1984; Tomlinson, 1982; Knebel, 1995; Tran et al., 1989; Denkmann, 1985; Hensel et al., 1991). Refrigerant gas hydrates are used as cooling storage systems, which have an appropriate melting temperature (277.15−280.15 K), a high specific storage capacity (302.4−464 kJ kg^{-1}) and a high heat transfer coefficient (Douglas, 1990; Ternes, 1983). Watanabe et al. (2004) and Ogawa et al. (2005) developed the refrigeration technology based on hydrate formation and dissociation.

For cooling storage applications, the dissociation conditions of refrigerant gas hydrates as well as suitable thermodynamic models should be available and be employed. Liang et al. (2001) published sets of equilibrium data for the hydrate dissociation relevant to some refrigerants, such as R-134a, R-141b and R-152a. Imai et al. (2005) reported hydrate equilibrium conditions for Difluoromethane in the presence of Cyclopentane or Tetra-n-butylammonium Bromide for usage in the hydrate-based refrigeration technology. Li et al. (2006) reported experimental data for the hydrate dissociation conditions related to R-134a in the presence of copper suspension nanoparticles and pure water. Because HCC, HCFC, HFC and FC chemicals are known to have greenhouse effects, these gases are target gases for emission reductions in the Kyoto protocol. Therefore, some researchers attempted to use CO_2 hydrate for the phase change material for the secondary refrigeration (Fournaison et al., 2004; Marinhas et al., 2006). Because the dissociation enthalpy of sII hydrate is much larger than sI hydrate and since the formation pressure of sII is less than sI, Delahaye et al. (2006) used the sII hydrate formed by CO_2 and THF for the secondary refrigeration system.

In the thermodynamic modeling of the refrigerant gas hydrates, Liang et al. (2001) obtained Kihara potential parameters for these refrigerants (R-134a, R-141b and R-152a) based on Holder et al.'s (1980) model. Recently, Eslamimanesh et al. (2011) developed a thermodynamic model for prediction of the hydrate dissociation conditions of some refrigerants.

The cubic equations of state (i.e., SRK, PR) often could not provide the accurately calculated volumetric property and the phase equilibrium data of complex mixtures containing hydrogen bonding compounds. This is because of the strong hydrogen bonding forces, which cannot be well considered by the corresponding terms of such EoS, especially when van der Waals fluid mixing rules are used. By using the statistical association fluid theory (SAFT) and some association EoS, this problem can be solved. The Cubic-Plus-Association (CPA) model is one of these applicable EoS (Kontogeorgis et al., 1996). CPA can predict the properties of pure compounds, as well as the mixtures of associating ones, such as water, alcohols, glycols and mixtures of them with hydrocarbons (Kontogeorgis et al., 2006a,b; Folas et al., 2005). Also, CPA EoS was successfully used for the prediction of hydrate dissociation conditions in absence of any aqueous phase (Youssef et al., 2009, 2010) and in the presence of thermodynamic inhibitors such as methanol and glycol (Haghighi et al., 2009a,b).

In their original work, van der Waals and Platteeuw (1959) used the Lennard-Jones 6-12 pair potential. They applied the Lennard-Jones potential more to monoatomic or spherical molecules than to oblate or polar molecules. The inaccurate prediction of this model leads to the fact that McKoy and Sinanoglu (1963) suggested the Kihara core potential was better for both large and non-spherical molecules. The Kihara potential function is normally used, with the parameters fitted to experimental hydrate dissociation data.

In this work, by using the cubic plus association equation of state and van der Waals −Platteeuw theory, hydrate dissociation conditions for refrigerant R-134a, R-141b and R-152a is modeled. Based on reference parameters for sI and sII, reported by Sloan (1990), Kihara potential Parameters for these materials are determined by an implicit least square optimization scheme. In this method, the difference between chemical potential of water in the hydrate and aqueous phases are calculated based on experimental hydrate dissociation conditions and then minimized by using a genetic algorithm.

2.   Thermodynamic modeling

2.1.   Cubic − plus −association EoS (CPA)

The cubic-plus-association model is an equation of state which combines the SRK (Soave-Redlich-Kwong) (Soave, 1972) cubic equation of state and association term derived from Wertheim theory (Wertheim, 1984a,b, 1986a,b; Huang and Radosz, 1990) as applied in SAFT (Huang and Radosz, 1990). The SRK model considers physical interaction between the molecules and the association term takes into account the specific site−site interaction stem from hydrogen bonding between similar molecules (self-association) and different ones (cross-association).

The CPA EoS can be expressed in terms of pressure as a summation of the SRK EoS and the contribution of association term, as suggested by Michelsen and Hendriks (2001):

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} - \frac{RT}{2v}\left(1 - v\frac{\partial \ln g}{\partial v}\right)\sum_{i=1}^{nc}x_i\sum_{A_i}\left(1 - X_{A_i}\right) \qquad (1)$$

where v is the molar volume, X_{Ai} is the fraction of A-sites on molecule i that do not form bond with other active sites.

X_{Ai}, which is the key property in the association term (Huang and Radosz, 1990), must satisfy Eq. (2)

$$X_{A_i} = \frac{1}{1 + \frac{1}{v}\sum_{j=1}^{nc}x_j\sum_{B_j}X_{B_j}\Delta^{A_iB_j}} \qquad (2)$$