CO$_2$ separation from the mixture of CO$_2$/H$_2$ using gas hydrates: Experimental and modeling

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ABSTRACT

Hydrate formation is a new technique to separate hydrogen from carbon dioxide. In this way, modeling and prediction of gas hydrate kinetics is very important. Several experiments have been conducted to study the hydrate formation from pure carbon dioxide and mixture of hydrogen and carbon dioxide in a stirred reactor in different temperatures, pressures and compositions. The mass transfer approach model was used to predict the mass transfer coefficient for each experiment, and the dependency of temperature and pressure has been studied. It was observed that the mass transfer coefficient of CO$_2$ in the mixture is close to the pure system. The result of this work shows that the pure data on the kinetics for CO$_2$ hydrate formation is applicable for the case of CO$_2$ separation from the mixture of carbon dioxide and hydrogen.

Introduction

Gas hydrates are crystalline compounds composed of water and gas molecules. This class of crystalline compound is known as clathrate. Within the clathrate lattice, water molecules compose a hydrogen-bonded network of, which have many cavities. Gas molecules are trapped in these cavities, and the combination of water and gas molecules form hydrate under low temperature and high pressure. Depending on the size and chemical characteristics of gas molecules, natural gas can form two types of hydrate structures (Structure I, II) [1,2].

Veluswamy and Linga studied the formation of hydrogen hydrates in the presence of tetrahydrofuran [3] as the thermodynamic promoter. Later, Veluswamy et al. investigated the capacity of gas hydrate to storage the hydrogen using tetrahydrofuran, tetra-*n*-butylammonium bromide and cyclopentane [4]. Sun et al. have prepared an experimental setup to separate H$_2$ and N$_2$ from tail gases of ammonia plant in the presence of tetra-*n*-butylammonium bromide [5].

One of the main sources of hydrogen in industry is the steam reforming of hydrocarbons in petrochemical plants. In these units, considerable energy is used to separate of H$_2$ and CO$_2$. CO$_2$ forms hydrate sI in the conditions of a few MPa and suitable temperatures, whereas H$_2$ forms hydrate sII in the conditions of more than 200 MPa or lower than 80 K [6]. At the same temperature, the hydrate equilibrium pressure of CO$_2$ is lower than H$_2$. Thus, CO$_2$ is expected to be preferentially entrapped into the cavities to form gas hydrates relative to hydrogen under the same conditions. Consequently, the CO$_2$-

rich steam can be withdrawn from the gas hydrates dissociation gases [7]. Although there some valuable work in the literature about the separation of H_2/CO_2 using gas hydrates [6,8], but modeling of hydrate kinetics is of prime to use this technique for separation processes.

In order to use this method, deep understanding of the kinetics of hydrate formation is required for modeling and predicting of gas uptake rate and quantity of separation. Many efforts have been done to predict and measure the kinetics of hydrate formation by researchers. Vysniauskas and Bishnoi [9] carried out the first attempt to examine the kinetics of hydrate formation. Afterwards, Englezos et al. [10] conducted experiments on the formation of hydrates methane and ethane. Accordingly, they proposed a model to predict the kinetic of hydrate formation. Gaillard et al. [11] presented an empirical correlation for methane hydrate. Skovborg and Rasmusen [12] presented a mass transfer model for hydrate formation on the basis of Englezos model. They considered that the resistance of mass transfer in gas-liquid interface determines the kinetic of hydrate. Xu et al. have been reported separation of CO_2 from flue gas using pilot-scale equipment. They have found the optimal gas to fluid flow rate, which has the highest separation [7].

In the present work, several experiments were conducted on hydrate formation of CO_2 and gas mixtures of CO_2/H_2 in order to obtain kinetic data at different pressures and temperatures in a stirred reactor. In the experiments, the consume gas by hydrate was measured. The mass transfer model [12,13] was used to determine the mass transfer coefficient (MTC) of CO_2 and CO_2/H_2. Mass transfer coefficients obtained can be used to predict the rate of gas uptake and quantity of separation in hydrate based gas separation.

Theory

There are several kinetic models to describe hydrate formation or dissociation on the basis of different driving forces [14]. As it was stated by Li et al., the rate of gas consumption by the hydrate phase can be described [15]:

$$\frac{dn_H}{dt} = ke^{-\frac{\Delta E}{RT}}A_S\left(f_g - f_{eq}\right) \tag{1}$$

In the above equation, n_H, t and k are moles in the hydrate phase, time and the mass transfer coefficient, respectively. The mass transfer coefficient has been presented similar to Arrhenius expression $\left(e^{-\frac{\Delta E}{RT}}\right)$. A_S shows the interfacial area between the gas and aqueous phases. The driving force has been defined as the difference between fugacities in the gas phase and equilibrium conditions. Resistance in the gas phase can be considered negligible due to low solubility of carbon dioxide in water [16]. So, fugacity in gas phase (f_g) is replaced by fugacity in the interface (f_i). Consequently, Eq. (1) can be rewritten as below:

$$\frac{dn_H}{dt} = ke^{-\frac{\Delta E}{RT}}A_S\left(f_i - f_{eq}\right) \tag{2}$$

When the solubility of gas in aqueous phase is low, Henry's law can be applied.

$$\frac{dn_H}{dt} = ke^{-\frac{\Delta E}{RT}}A_S\left(H_i x_i - H_{eq} x_{eq}\right) \tag{3}$$

where H is the Henry's law constant. Also, it can be assumed that (at constant temperature) the Henry's law constant does not change significantly with pressure change when the change is not high [17]. Accordingly:

$$\frac{dn_H}{dt} = ke^{-\frac{\Delta E}{RT}}A_S H\left(x_i - x_{eq}\right) \tag{4}$$

On the basis of mass transfer approach model, most of the mass transfer resistance stands at the liquid side of gas–liquid interface. Hence, A_S represents practically contact area among gas and liquid phase (A_{V-L}) [12,15,18].

Eventually, when temperature is constant, Eq. (7) can be rewritten as bellow:

$$\frac{dn_H}{dt} = A_{V-L}C_W k_L\left(x_i - x_{eq}\right) \tag{5}$$

where, C_W represents water concentration. Henry's law was employed to determination of x_i and x_{eq}.

$$y_i P \varphi_i^v = x_i H_i \tag{6}$$

where φ, y and H are the fugacity, composition and Henry's law constant of component i in the vapor phase, respectively. Krichevsky–Kasarnovsky equation (Eq. (7)) was used to determination Henry's law constant [19].

$$\ln H_{2,1} = \ln H_{2,1}^{(p_1^s)} + \frac{\overline{v}_2^\infty\left(p - p_1^s\right)}{RT} \tag{7}$$

where $\overline{v}_i^\infty$ is the partial molar volume of solute i (here carbon dioxide) in the liquid phase (water) at infinite dilution and $H_{i,solvent}^{(p^r)}$ is Henry's constant calculated at arbitrary pressure p^r (usually vapor pressure). For carbon dioxide, Eqs. (8) and (9) were used to calculation of $\overline{v}_i^\infty$ [20] and $H_{2,1}^{(p_1^s)}$ [21].

$$H_{2,1}^{(p_1^s)} = 10\exp\left[-6.8346 + 1.2817 \times 10^4\left(\frac{1}{T}\right) - 3.7668 \times 10^6\left(\frac{1}{T^2}\right)\right.$$
$$\left. + 2.997 \times 10^8\left(\frac{1}{T^3}\right)\right]0 \tag{8}$$

$$\overline{v}_2^\infty = 1799.36 - 17.821\,T + 0.6592\,T^2 - 1.0579 \times 10^{-4}T^3 + 6.2$$
$$\times 10^{-8}T^4 \tag{9}$$

In which, R is universal gas constant (8.314×10^{-3} kJ/mol. K) and H and P are in kPa. In order to estimate the properties of gas (fugacity and compressibility factor), SRK equation of state [22] was used in this work. x_i and x_{eq} were calculated in operating temperature (T) and operating pressure (Pop) and corresponding equilibrium pressure with respect to T (Peq), respectively. Experimental data of CO_2 and CO_2/H_2 were applied to rightfully estimate the equilibrium conditions of hydrate formation [1,23]. Therefore, some third-order polynomial equations were proposed to determinate equilibrium pressure. The coefficients of Eq. (10) presented in Table 1.