

A Study on Thermodynamic Properties of Ethylene Gas Hydrate

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Abstract

The gas hydrates are probably most sensitive to climate change since they are stable only under specific conditions of high pressure and low temperature. One of the main factors responsible for formation of gas hydrates is the saturation of the gases with water vapor. Quantitative phase equilibrium data and understanding of the roles of water component in the phase behavior of the heterogeneous water-hydrocarbon-hydrate mixture are of importance and of engineering value.

In this study, the water content of ethylene gas in equilibrium with hydrate and water phases were analyzed by theoretical and experimental methods at temperatures between 274.15 up to 291.75 K and pressures between 593.99 to 8,443.18 kPa. The experimental and theoretical enhancement factors (EF) for the water content of ethylene gas and the fugacity coefficients of water and ethylene in gas phase were determined and compared with each other over the entire range of pressure carried out in this experiment. In order to get the theoretical enhancement factors, the modified Redlich-Kwong equation of state was used. The Peng-Robinson equations and modified Redlich-Kwong equations of state were used to get the fugacity coefficients for ethylene and water in the gas phase.

The results predicted by both equations agree very well with the experimental values for the fugacity coefficients of the compressed ethylene gas containing small amount of water, whereas, those of water vapor do not in the ethylene rich gas at high temperature for hydrate formation locus.

Key words : Gas hydrates, Ethylene, Fugacity coefficient

1. INTRODUCTION

Gas hydrates are similar in appearance to wet snow or to dry ice and are stable only under specific high pressure and low temperature conditions. Therefore, they may be the first exploited and probably the most sensitive to climate change (Hornbach *et*

al., 2004). In addition, the rate of hydrate formation depends on the rate of change in the moisture content of the gas that occurs with the change in pressure and temperature. There are several such components which can form their hydrates under proper conditions for the hydrate formation. Ethylene gas (C₂H₄, Ethene) is one of them (Sugahara *et al.*, 2000).

Ethylene is the simplest alkene hydrocarbon and produced by steam cracking in the petrochemical

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industries and a component of natural gas. Ethylene is used as a hormone in plants. It stimulates the ripening of fruit, the opening of flowers, and the abscission of leaves (Akiya, 1991). It has been also known as a greenhouse gas much more effective than carbon dioxide in causing climate warming.

The employment of these studies depends on the conditions of hydrate formation and on the specific place where it occurs in the complex system of gas production, transportation, and utilization (Kvenvolden and Lorensen, 2001). As mentioned above, one of the main factors responsible for formation of gas hydrates is the degree of water vapor saturation in the gas phase (Lu *et al.*, 2000). Quantitative phase equilibrium data and understanding of the roles of these factors in the phase behavior of the heterogeneous water-hydrocarbon-hydrate mixture are of importance and of engineering value. Therefore, in order to determine the conditions of hydrate formation of gas, we must know the gas moisture content and also changes therein depending on pressure and temperature. The water to gas ratio in the hydrate phase which resemble wet snow is also dependent

on the equilibrium gas phase composition, pressure, and temperature. Several workers (Dipen and Cleef, 1962; Dipen and Scheffer, 1950) have determined phase equilibrium data for ethylene-water system. But ethylene gas hydrate was first obtained by Villard [11], who determined dissociation pressures of 557.15 and 4,538.24 kPa for the hydrate at 0 and 17°C, respectively. The water content of the gaseous phase (Kobayashi and Katz, 2004) is considerably greater than that of the liquid phase due to the hydrogen bonding nature of water and is strongly influenced by the fluid state. The presence of water in a mixture shifts the mixture composition of the dew point at a given temperature and pressure (Lim, 2006; Kobayashi and Katz, 2004).

2. EXPERIMENTAL EQUIPMENT AND METHODS

Experiments in this study were conducted to determine the three-phase of vapor (V)-hydrate (H)-water rich liquid (L₁) and the two-phase of vapor (V)-hyd-

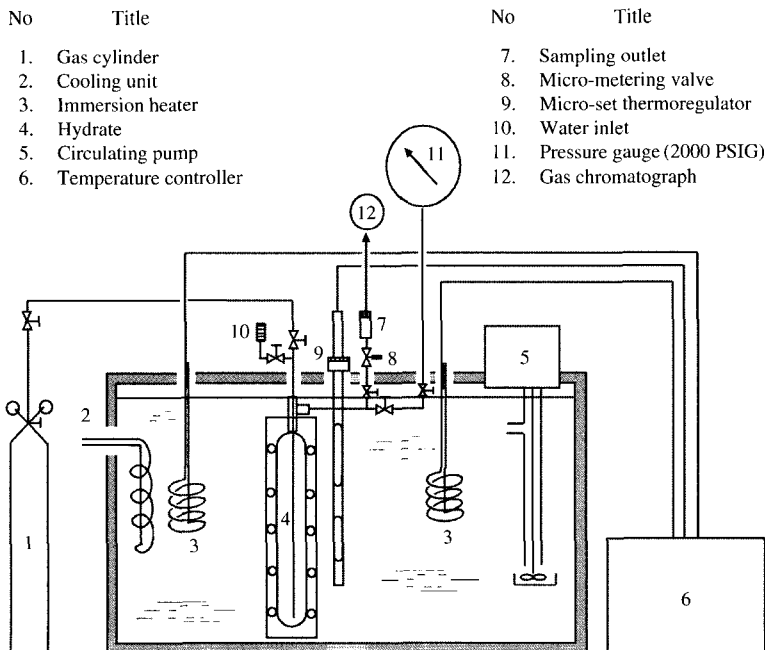


Fig. 1. Schematic diagram of experimental apparatus.

rate (H) or vapor (V)-water rich liquid (L_1) equilibrium conditions for ethylene hydrate. The pressure and temperature at which hydrate was formed were measured for ethylene equilibrium gas. Hydrate existence was determined by visual observation through a glass windowed high pressure cell. Gas phase composition were also measured by using Gas Chromatograph (Shimadzu GC-FID) at various conditions. Chilled mirror hygrometer (MBW-373) was used to measure water vapor.

2.1 Experimental equipment

The experimental apparatus consisted of hydrate cell, a pressure gauge, a micro-set thermoregulator, a circulating pump, two heaters, a refrigeration unit for measuring hydrate forming conditions in this work as shown in Figure 1. The pressure and temperature measurements were determined to be accurate to the absolute value of 1.25 psia and 0.05°C, respectively. The inside volume of the main cell was 100 cm³. Since the main cell had glass windows on both sides of the hydrate chamber, the entire contents of the chamber were always visible. The inlet section of the system had a gas cylinder of ethylene which had a purity of 99.8 mol%. The gas could be passed through the inlet section of the tubing into the hydrate cell where the hydrate formation took place. The outlet line could be connected to a vacuum pump which could evacuate the system to 0.03 psia. Tubings and valves were all made of 316 stainless were of standard 0.3175 cm (1/8 inch) size.

2.2 Experimental methods

The separation columns for GC used in this study were packed with 80/100 porapak-s packing. Helium was used as a carrier gas at the flow rate of 25 cc/min. The GC column was also conditioned at room temperature for 30 minutes and then at 150°C overnight whenever the helium cylinder was changed.

To determine the response factors of pure water-vapor and ethylene for a standard gas chromatography with a thermal conductivity detector used in this study, pure water-vapor and ethylene were analyzed in the regular interval between the analysis of equilibrium gas samples. The average value of the

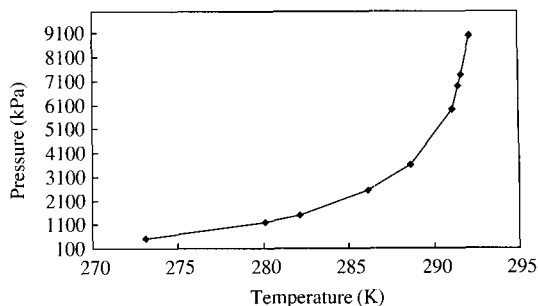


Fig. 2. Ethylene hydrate dissociation curve.

response factors of pure ethylene was 1.122×10^{-7} gr-gmol/area. The aluminum oxide moisture sensor of hygrometry was used to measure moisture in gas phase. Dew and frost point range of the hygrometry is in -100°C to 20°C or 1.6 ppbv to 23,000 ppmv.

3. RESULTS

3.1 Hydrate dissociation curve of ethylene

The P-T relations of the three-phase equilibria of Vapor (V)-Water rich liquid (L_1)-Hydrate (H) in the system of ethylene-water were determined from 274.15 to 291.75 K and from 593.99 to 8,443.18 kPa in the range of temperature and pressure, respectively. The experimental hydrate dissociation data which are shown in Figure 2 are in good agreement with those obtained by other workers (Sugahara *et al.*, 2000; Dipen and Cleef, 1962). Because the critical point, $T_c=282.5$ K and $P_c=5,115.65$ kPa, of ethylene is above the three-phase curve (VL₁H), only the single hydrocarbon phase exists and there is no region of two immiscible liquids (Gnanendran and Amin, 2003). For this region the ethylene-water system does not have a quadruple locus corresponding to the hydrate (H)-vapor (V)-water rich liquid (L_1)-hydrocarbon rich liquid (L_2) equilibrium.

3.2 Water content of ethylene gas in equilibrium with hydrate and water phases

Experimental data were obtained for the water content of ethylene gas in equilibrium with hydrate

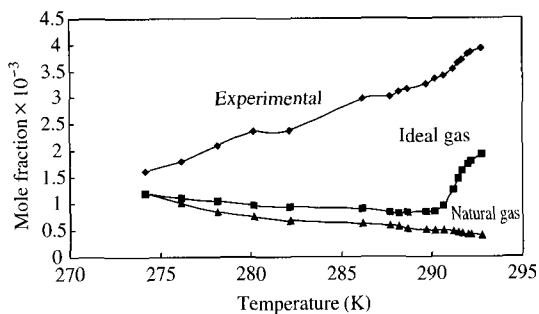


Fig. 3. Water solubility of ethylene gas along with hydrate formation temperature locus.

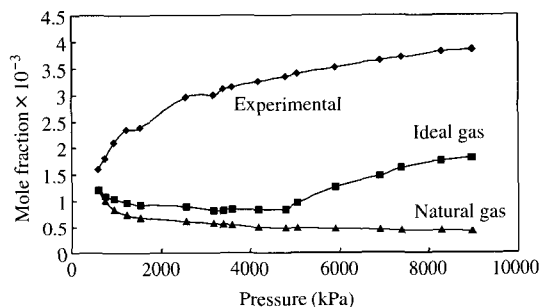


Fig. 4. Water solubility of ethylene gas along with Hydrate formation pressure locus.

and water phases. The water concentration in the gas phase along with the hydrate formation locus are presented in Figure 3 and 4. Also included in Figure 3 and 4 are two curves showing the water content of natural gas (Katz *et al.*, 2004) and the water concentrations as calculated by treating the water vapor as an ideal gas ($f=yp$) at the system conditions.

The maximum water content in the gas phase was 0.0038 mole fraction and this amount of water is more than twice as much as we would expect on the basis of the ideal gas law. The maximum value will be definitely extended as pressure and temperature for hydrate formation are increased in the limited range. This solubility phenomenon may be more a function of temperature than the chemical affinity between the ethylene and water (Slon *et al.*, 1976). On the other hand, the equilibrium solubility of a

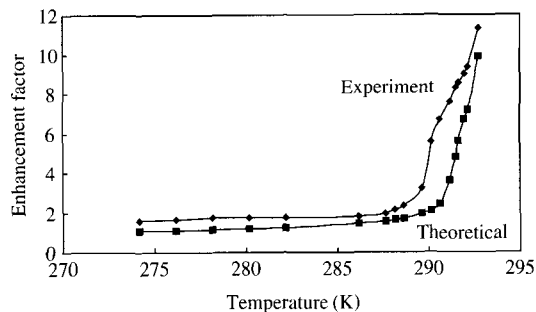


Fig. 5. Enhancement factor for water solubility in the gas phase with hydrate formation locus.

substance in a gas is generally greatest when the system temperature is closer to the critical temperature of the gaseous fluid (Katz *et al.*, 2004).

3.3 The enhancement factors and fugacity coefficients for water solubility of ethylene gas

It is also useful to describe the solubility in terms of an enhancement factor (EF) which is the ratio of the actual gas solubility to the ideal gas solubility as the following equation (Redlich *et al.*, 1965).

$$EF = \frac{Py_w}{P_w^o}$$

where P_w^o is the saturation vapor pressure of pure water at the same temperature, P is the system total pressure, and y_w is the mole fraction of water in the vapor phase. The theoretical enhancement factors are also obtained by using the following equation (Redlich *et al.*, 1965) and compared with experimental values as shown in Figure 5.

$$EF = \frac{\Phi_w^o \exp \int_{P_w^o}^P \frac{V}{RT} dP}{\Phi_w}$$

where the enhancement factor contains three correction terms, that is, Φ_w^o , which takes into account nonideality of the pure saturated water vapor, the Poynting correction which gives the effect of pressure on the fugacity of the pure water, and Φ_w , the vapor phase fugacity coefficient in the high pressure

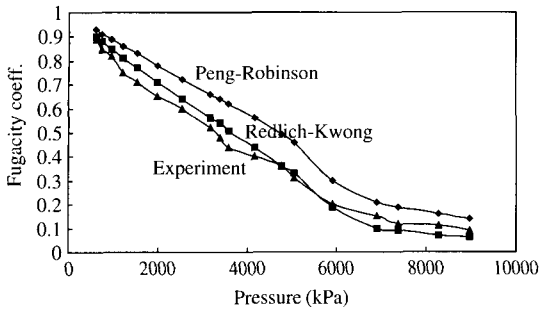


Fig. 6. Fugacity coefficients of water in the gas with hydrate and water.

gas mixture which was calculated using the modified Redlich-Kwong and Peng-Robinson equation of states which are as follows, respectively.

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$$

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

The theoretical fugacity coefficients were calculated by applying equations of state to the general thermodynamic relationship:

$$\ln \Phi_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{P} \right] dP$$

The gas-phase fugacity coefficients of water (Φ_w) shows also somewhat deviations between estimated values and calculated values as shown in Figure 6. Nonideal behavior of the water-ethylene-hydrate system at low pressure is not large because the fugacity coefficients of ethylene are still near the order of magnitude of unity.

4. DISCUSSION AND CONCLUSION

The observed high solubility of water vapor in the gas phase may be due to the stronger function of temperature than the chemical affinity between the ethylene and water. The deviation of EF between the experimental and theoretical values results from gas-phase nonideality above the critical point. But

the trend results in fair agreement of the equation of the state to account for gas-phase nonideality. Although the deviation of fugacity coefficients are not large, solubility of water in ethylene gas phase increased as the locus of hydrate formation is extended. All the properties of the fluid near the critical condition should, in principle, be obtained from molecular physics. Therefore, it is hard to predict properties of the fluid of polar molecules due to incomplete knowledge of intermolecular forces between such complicated molecules. The small deviation at low density may increase to big errors as the fluid density increases. The modified Redlich-Kwong and Peng-Robinson equations fit the experiment fugacity coefficient curve of ethylene for vapor phase, whereas those equation do not fit the curve for water vapor in ethylene. It was verified again that those equations could be applied with acceptable results to nonpolar components of a mixture containing a small amount of polar component.

Based on the results of this study, the more accurate model should be developed to predict the water solubility along with the hydrate formation locus in the future.

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