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Measurement of Dissolved Propane in Water in the Presence of Gas Hydrate

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The concentration of propane dissolved in water in the presence of propane gas hydrates has been measured at temperatures from (274 to 277) K and pressures from (150 to 350) kPa. Solubility measurements in the absence of hydrate were found to be in agreement with literature values, which predict an increase in solubility as temperature is decreased. In the hydrate formation region, the solubility of propane decreased with decreasing temperature. Therefore, hydrate formation reverses the gas−liquid solubility trend. Results also show that pressure does not have a strong influence on solubility in the presence of gas hydrate.

Introduction

Gas hydrates, or clathrate hydrates, are nonstoichiometric crystalline compounds in which individual guest molecules of a suitable size and shape are caged inside a network of hydrogen-bonded water molecules. The water network is stabilized by weak van der Waals forces between the host and the internal guest molecules. Clathrate hydrates, containing mostly natural gas, occur in vast quantities within and below the permafrost zone and in subsea sediment where the existing pressures and temperatures allow for thermodynamic stability of the hydrate.[1] Conservative estimates indicate that approximately 10^{16} kg of carbon is trapped in oceanic sediments in the form of hydrates,[2] which far exceeds any existing hydrocarbon reserve on the planet.

It is important to study gas hydrates not only because of the large potential they possess as a future energy source but also because of the problems they pose to the petroleum industry during the production, transportation, and processing of natural gas and oil.[3] Although most hydrate research focuses on methane, the primary component of natural gas, propane is another component of natural gas that is known to physically combine with water under certain temperature and pressure conditions to form hydrates.[1] For storage and transportation of liquefied petroleum gases (LPGs), composed mainly of propane and butane, it is important to know and to be able to predict the conditions of hydrate formation in the presence of humidity or ice.[4]

Propane forms structure II hydrate when combined with water under correct thermodynamic conditions. In the propane + water system, the location of the two quadruple points occurs at relatively low pressures ($P_{Q_1} = 1.5$ bar and $P_{Q_2} = 6.0$ bar) with the upper quadruple point existing at a relatively low temperature ($T_{Q_2} = 279$ K) in comparison with other hydrate formers (see Figure 1).[5] The nearly vertical $H-L_w-L_{C_3H_8}$ equilibrium line restricts hydrate formation to temperatures just above T_{Q_2}. Therefore, although propane hydrate occurs at modest pressures and temperatures, the thin borders of the formation region restrict hydrate formation potential.

For modeling and prediction of hydrate formation conditions, knowledge of thermodynamics and kinetics of hydrate formation are required. In particular, accurate solubility measurements in the hydrate formation region may enhance our understanding of hydrate formation kinetics.[6] The objective of the present study is to measure the solubility of propane in the aqueous phase in the presence of gas hydrate.

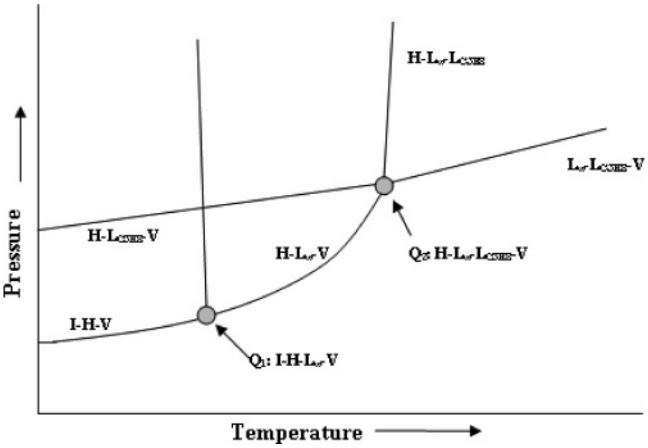

Figure 1. Partial phase diagram for the water + propane system where L_w represents liquid water; $L_{C_3H_6}$ is liquid propane; V is vapor; H is hydrate; and I is ice. Q_1 and Q_2 represent the two quadruple points of the system.[5]

Experimental Apparatus

The primary component of the hydrate equilibrium apparatus was a high-pressure crystallizer, shown in Figure 2 and constructed of 316 stainless steel. The crystallizer had two circular viewing windows in the front and back and was equipped with a top mount Dyna/Mag magnetic mixer with revolutions per minute control capable of agitation at speeds up to 2500 rpm (Pressure Product Industries, Warminster, PA). A series of variable-volume reservoirs and a Baumann 51000 series low-flow control valve (Laurentide Control, Montreal, QC) were used to hold the crystallizer pressure constant during experiments. Pressure measurements were made with model 3051S Rosemount pressure transducers (Laurentide Control, Montreal, QC), programmed for pressure measurements over a range of (0 to 13 789) kPa with a reference accuracy of less that 0.065 % of the span. The temperature inside the top and bottom of the crystallizer was monitored by Omega high-accuracy RTD probes. The crystallizer and reservoir were all immersed in an insulated bath consisting of a 20 % glycol + water mixture. Temperature and pressure measurements were

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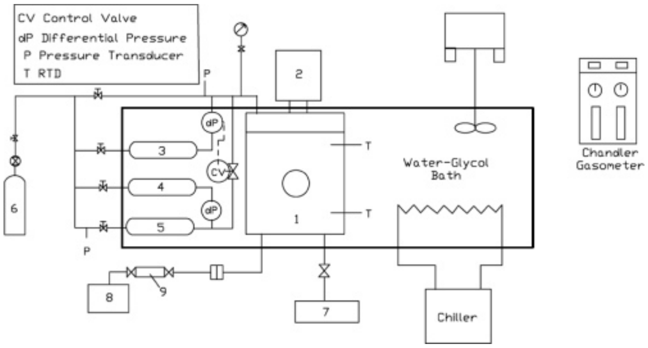

Figure 2. Schematic diagram of the experimental solubility apparatus: 1, crystallizer; 2, mixer; 3, bias reactor; 4, bias reservoir; 5, feeding reservoir; 6, propane tank; 7, positive displacement pump; 8, vacuum pump; 9, sample cylinder.

Table 1. Mole Fraction of Propane in Water, x_1, at Given Temperatures and Pressures

T/K	P/kPa	10^4x_1	region[a]
274.21	150	1.118	V−L_w
274.18	188	1.440	V−L_w
274.25	200	1.417	V−L_w
275.17	201	1.243	V−L_w
275.15	250	1.502	V−L_w
276.21	250	1.445	V−L_w
274.23	253	1.439	H−L_w
276.20	301	1.702	V−L_w
274.16	301	1.440	H−L_w
275.20	302	1.572	H−L_w
275.20	352	1.572	H−L_w
276.16	355	1.642	H−L_w
274.33	358	1.546	H−L_w

[a] H, L_w, and V refer to solid hydrate, liquid water, and vapor, respectively.

obtained via a PC equipped with Labview and a National Instruments data acquisition system.

An automated high-pressure positive displacement pump (Schlumberger Canada Ltd., Edmonton, AB) was used to displace the gas volume in the reactor at constant pressure to achieve two-phase hydrate−liquid water equilibrium. A high-pressure filter assembly (Millipore, Bedford, MA) was used when necessary to ensure that the liquid samples being analyzed did not contain any hydrates. The assembly is capable of withstanding a 20 MPa difference across the filter and removes all particles greater than 10 nm in diameter. A digital gasometer (Chandler Engineering, Tulsa, OK) with an accuracy of 0.2 % of the reading was used to measure the volume and temperature of gas expanded from the liquid sample bomb.

Procedure

The hydrate crystallizer was filled with 250 mL of distilled and deionized water. High-purity propane (99.5+ %, MEGS, Montreal, QC) was supplied from the gas bottle until the desired pressure was obtained, and propane addition to the crystallizer continued throughout the experiment to ensure constant pressure inside the crystallizer. The experimental results of Deaton and Frost were used to determine the three-phase H−L_w−V points for the propane + water system.[7] The procedure for the measurement of the concentration of dissolved propane in the aqueous phase was dependent on which region of the phase diagram the experiment was conducted. If the experiment was carried out below the three-phase line in the two-phase V−L_w equilibrium, a liquid sample was collected in an evacuated sample bomb that was removed from the apparatus once it had reached equilibrium. If the experiment was conducted above the three-phase line in the H−L_w equilibrium region, the gas volume in the reactor must be displaced with water while maintaining constant pressure in the presence of hydrates. After equilibrium had been obtained between the liquid water and hydrate phases, a hydrate-free liquid sample was then collected in the evacuated sample bomb for analysis. Figure 3 shows the set of experimental conditions at which propane solubility in water was measured in this study.

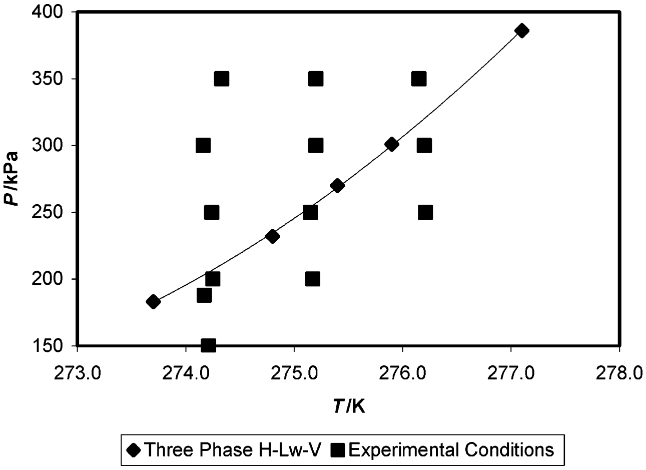

Figure 3. Partial phase diagram for the propane + water system. The line represents the three-phase H−L_w−V equilibrium line.[7] Below the line, gaseous propane and liquid water coexist at equilibrium, and above the line, liquid water and propane hydrate may exist at equilibrium.

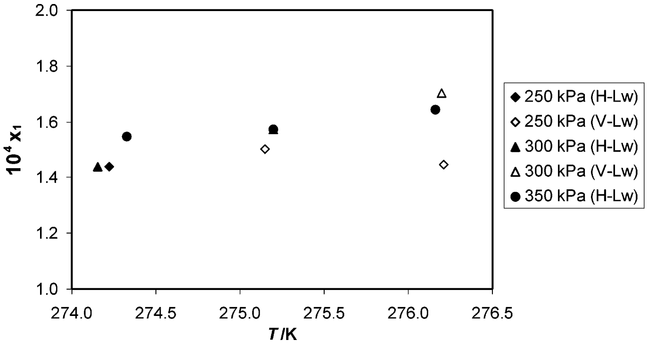

Figure 4. Plot of equilibrium mole fraction of propane, x_1, as a function of temperature at 250 kPa, 300 kPa, and 350 kPa, respectively (three phase H−L_w−V equilibrium temperatures are 275.2 K, 276.0 K, and 276.7 K, respectively).

An analytic flash technique was used to determine the concentration of propane dissolved in the liquid sample.[6,8] Using the gasometer, the contents of the sample bomb were brought to room temperature and atmospheric pressure. The gasometer accomplishes this by allowing the propane to evolve from the sample bomb into a floating piston where the gas volume and temperature were measured and recorded. The moles of propane, n_1, in the vapor phase in the gasometer were then calculated by

$$n_1 = (P - P^{V}_{H_2O})\frac{V}{ZRT} \tag{1}$$

where P, V, R, T, and Z are the atmospheric pressure, volume of the vapor in the gasometer, universal gas constant, room temperature, and compressibility factor for propane, respectively.

Table 2. Comparison of the Experimentally Determined Solubility in the Two-Phase Vapor−Liquid Water Region to Those Calculated Using the Correlations of Carroll and Mather[11] and Chapoy[13]

T/K	P/kPa	10^4x_1	10^4x_1(calcd)[a]	10^4x_1(calcd)[b]	$100(x_1^a - x_1)/x_1^a$	$100(x_1^b - x_1)/x_1^b$
274.18	188	1.440	1.334	1.363	−8.0	−5.7
274.21	150	1.118	1.063	1.086	−5.2	−2.9
274.25	200	1.417	1.417	1.447	0.0	2.1
275.15	250	1.502	1.690	1.725	11.1	12.9
275.17	201	1.243	1.357	1.386	8.4	10.2
276.21	250	1.445	1.611	1.644	10.3	12.0

[a] Using Carroll's correlation for Henry's constants. [b] Using Chapoy's correlation for Henry's constants.

Values for Z were obtained from the Trebble−Bishnoi equation of state.[9] $P_{H_2O}^V$ is the vapor pressure of water at the vapor temperature. Because the liquid sample volume and the solubility of propane in water at room temperature and atmospheric pressure are known,[10,11] the mole fraction of propane, x_1, dissolved in the aqueous phase at the experimental conditions can be calculated using the following equation

$$x_1 = \frac{\dfrac{x_1' n_2}{1 - x_1'} + n_1}{\dfrac{x_1' n_2}{1 - x_1'} + n_1 + n_2} \tag{2}$$

where x'_1 is the mole fraction of propane dissolved in water at room temperature and atmospheric pressure and n_2 is the number of moles of water in the sample bomb. Because the volume of the sample bomb was known, n_2 can be calculated using steam tables[12] at the experimental temperature and pressure.

Results and Discussion

Experiments were conducted over a range of (274 to 277) K and (150 to 350) kPa in both the vapor−liquid water and hydrate−liquid water equilibrium regions. A series of replicate experiments at each temperature and pressure condition were performed with a maximum absolute average deviation from the mean of 4.6 %. The mean results at each temperature and pressure condition are presented in Table 1, and measurements at 250 kPa, 300 kPa, and 350 kPa, respectively, are plotted in Figure 4. Also, in Table 2, the measurements taken in the vapor−liquid water region are presented and compared to the correlation of Carroll and Mather[11] and the correlation of Chapoy.[13] As expected, propane solubility in the absence of hydrate increases with decreasing temperature, and the results obtained are close to literature values.

The results for the solubility of propane in the presence of propane hydrate show that at a given pressure the solubility of propane in water decreases as the temperature decreases in the hydrate formation region. Therefore, the formation of gas hydrate reverses the gas−liquid solubility trend. This is in agreement with the conclusions of Ohmura and Mori[14] and Servio and Englezos.[6,8] Furthermore, it can be seen that solubility is not a strong function of pressure in the hydrate formation region.

Conclusions

The solubility of propane in water in the hydrate formation region was measured using an analytical flash technique for temperatures ranging from (274 to 277) K and pressures of (150 to 350) kPa. Solubility results show that the amount of propane dissolved in water decreases with decreasing temperatures in the hydrate formation region. Furthermore, solubility was not found to be a strong function of pressure in the hydrate formation region.

Literature Cited

(1) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*; Marcel Dekker: New York, 1998.

(2) Buffet, B. A. Clathrate Hydrates. *Annu. Rev. Earth Planet Sci.* **2000**, *28*, 477−507.

(3) Englezos, P. Clathrate Hydrates. *Ind. Eng. Chem. Res.* **1993**, *32*, 1251−1274.

(4) Giavarini, C.; Maccioni, F.; Santarelli, M. L. Formation Kinetics of Propane Hydrates. *Ind. Eng. Chem. Res.* **2003**, *42*, 1517−1521.

(5) Mooijer, M. M.; Peters, C. J.; De Swaan Arons, J. Gas Hydrate Phase Equilibria for Propane in the Presence of Additive Components. *Fluid Phase Equilib.* **2002**, *193*, 245.

(6) Servio, P.; Englezos, P. Measurement of Dissolved Methane in Equilibrium with its Hydrate. *J. Chem. Eng. Data* **2002**, *47*, 87−90.

(7) Deaton, W. M.; Frost, E. M., Jr. Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines. Monograph for US Dept. Interior, 1946.

(8) Servio, P.; Englezos, P. Effect of Temperature and Pressure on the Solubility of Carbon Dioxide in Water in the Hydrate Formation Region. *Fluid Phase Equilib.* **2001**, *190*, 127−134.

(9) Trebble, M. A.; Bishnoi, P. R. Development of a new four parameter equation of state. *Fluid Phase Equilib.* **1987**, *35*, 1−18.

(10) Yaws, C. L. Henry's Law Constant for Compound in Water. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*; http://www.knovel.com, 2003.

(11) Carroll, J. A Model for the Solubility of Light Hydrocarbons. *Chem. Eng. Sci.* **1997**, *52*, 4, 545−552.

(12) Perry, R. H.; Green, D. W. *Perry's Chemical Engineering handbook*, 7th ed.; McGraw-Hill: New York, 1997.

(13) Chapoy, A.; Mokraoui, S.; Valtz, A.; Richon, D.; Mohammadi, A. H.; Tohidi, B. Solubility and modelling for the propane water system from 277.62 to 368.16 K. *Fluid Phase Equilib.* **2004**, *226*, 213−220.

(14) Ohmura, R.; Mori, Y. H. Comments on "Solubility of Liquid CO_2 In Synthetic Sea Water at Temperatures from 278 K to 293 K and Pressures from 6.44 MPa to 29.49 MPa, and Densities of the Corresponding Aqueous Solutions". *J. Chem. Eng. Data* **1999**, *44*, 1432−1433.

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