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Liquid Propane + Water Phase Equilibria at Hydrate Conditions

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An analysis of the results of measurement of phase transitions in the system propane + water in the region of hydrate formation is presented. A number of special kinetic features of the system are revealed. The equilibrium conditions of dissociation of liquid propane hydrate at pressures up to 35 MPa have been determined.

Introduction

Propane (along with methane, ethane, and butane) is one of the most common components of oil and natural gas. It is evident from the diagram shown in Figure 1 that propane has the highest specific energy content of hydrocarbons. Many studies have been devoted to hydrates of propane, the first by Villard.[1] The region of interest is primarily pressures from (0.1 to 1500) MPa and temperatures from (235 to 334) K. Analysis of the data published by different researchers shows significant disagreement. Table 1 and Figure 2 give the dissociation conditions of liquid propane hydrate reported by Wilcox et al.,[2] Reamer et al.,[3] Verma,[4] Robinson et al.,[5] and Berecz et al.[6] and predicted using software from Robinson[5] and Sloan.[7]

Figure 3 shows the propane hydrate dissociation curve at high pressures.[8] Data given in Table 1 and in Figure 2 show significant disagreements between authors for the phase equilibrium for liquid propane + water under hydrate formation conditions. Hydrate dissociation data have been measured in the range of temperatures from (−12 to +30) °C, at pressures to 35 MPa, for the purpose of refinement of the phase equilibria of the system liquid propane + water. The obtained results are presented in this work.

Experimental Section

The experimental equipment used in this research was constructed at Texas A&M University for the express purpose of studying phase transitions in water + gas systems at pressure up to 50 MPa. This equipment allowed us to examine the equilibrium pressure−temperature conditions of hydrate over the temperature range from (200 to 320) K, the kinetics and morphology of hydrates in both static and in dynamic conditions with a high degree of accuracy, the solubility of gas in water before and after hydrate formation, the rate of growing and dissolution of hydrate crystals in water under hydrate formation conditions, and more.

The cells had two sapphire windows of 64 mm diameter and a working volume from (160 to 210) cm^3. The windows provided the capability of observing and recording photographically the morphology of hydrate crystals in any location inside the cells. Working cells were housed in a liquid (WR Scientific US Co.) thermostat or air bath (Thermotron Co.), which were controlled by a programmed heater and refrigerator that allowed us to maintain the temperature within ±0.1 K. A high-resolution digital camera mounted on a Nikon microscope allowed us to capture the results in real time on a computer, in the form of photographs and videotape, so that information concerning the formation and dissociation, kinetics, and morphology of hydrate crystals was recorded.

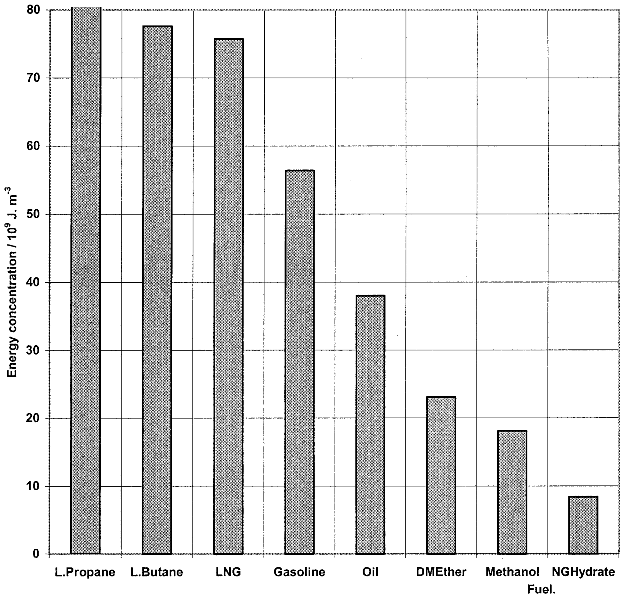

Figure 1. Specific energy concentration in fuel.

Table 1. Equilibrium Data on Propane Hydrate

Wilcox at al.[2]		Reamer et al.[3]		Verma[4]	
t/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa
5.8	0.807	1.17	0.248	5.3	0.562
5.5	1.296	2.55	0.312	5.32	3.87
5.5	1.758	4.05	0.424	5.40	7.03
5.7	2.034	5.44	0.70	5.50	11.3
6.1	2.902	5.50	1.515	5.40	16.8
5.7	4.247	5.61	2.098		

The pressure was monitored using precision Omega transducers with an accuracy of ±0.005 MPa. Constant working pressure was maintained in the cell using a Ruska digital press with an accuracy of 0.007 MPa. This accuracy was sufficient for measuring phase transitions of gas + water systems at hydrate conditions. Temperature was measured using an Omega digital thermometer, with an accuracy of ±0.01 K. Most parameters were recorded using

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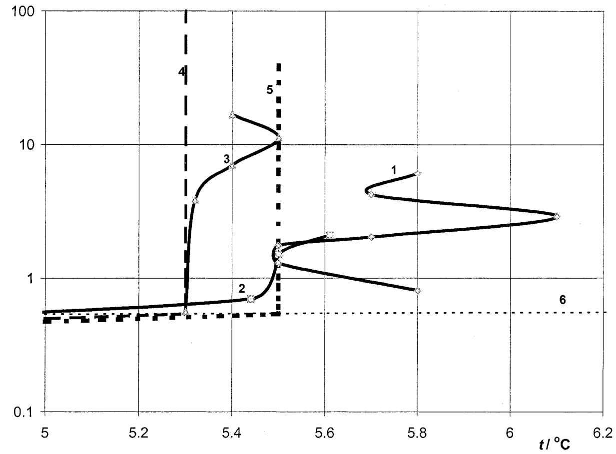

Figure 2. Liquid propane + water hydrate $P-t$ equilibrium dissociation by different researchers: 1, Wilcox; 2, Reamer; 3, Verma; 4, Robinson; 5, Sloan; 6, propane vapor pressure.

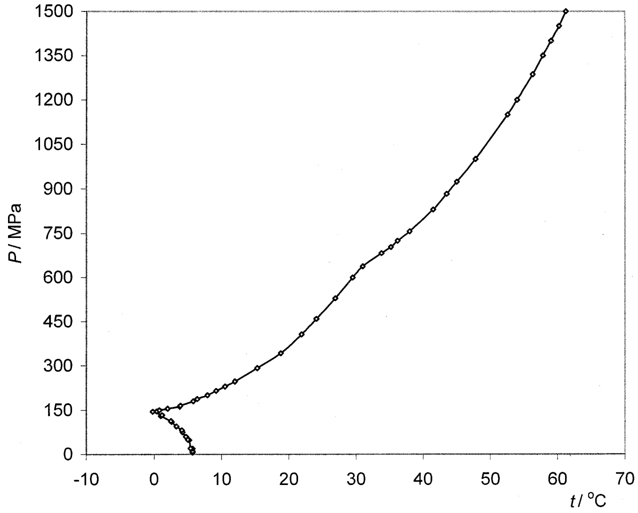

Figure 3. Liquid propane + water hydrate $P-t$ dissociation.

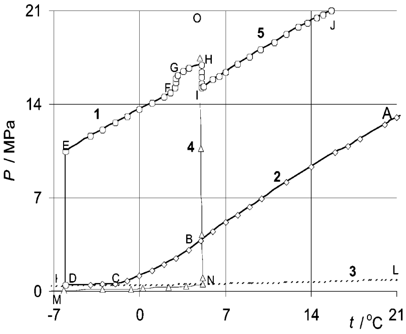

Figure 4. Propane + water hydrate formation and dissociation: 1, cooling; 2, heating; 3, vapor pressure; 4, equilibrium; 5, isochore.

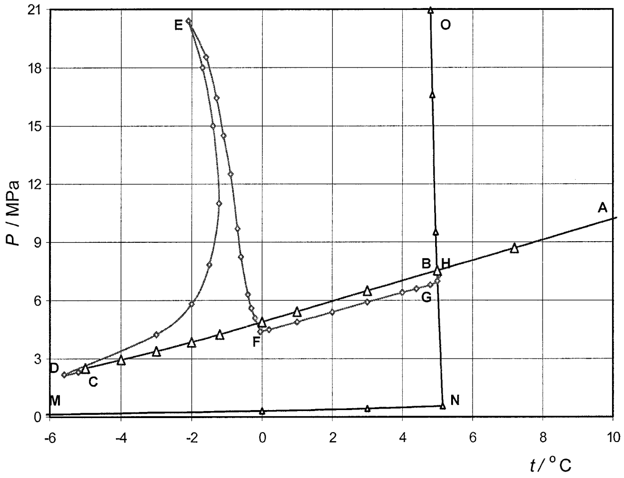

Figure 5. Propane hydrate and ice formation and dissociation.

a computer data acquisition system, along with video and photographs.

When considering phase equilibrium for hydrate of C_3H_8 for this work we used pure water and pure propane (99.95%).

The parameters that were controlled during the tests were as follows: compositions of the hydrate forming gas and water; pressure; temperature; rate of temperature and pressure change; and degree of fluid supercooling at the moment of hydrate formation and dissociation onset.

Other measured parameters were as follows: rate of hydrate decomposition as the temperature was increased or pressure changed; degree of temperature increase at the onset of hydrate formation; amount of pressure change during hydrate formation and dissociation; and rate of change of pressure with freezing water after hydrate formation.

Equilibrium $P-t$ Conditions for Water + C_3H_8 Hydrate

Propane forms hydrate structure II at tested conditions. The unit cell is a structure consisting of 136 molecules of water with 16 small and 8 large cavities. The composition of the hydrate corresponds to the formula $8M\cdot136H_2O$ or $M\cdot17H_2O$.[9]

The enthalpy of hydrate dissociation near ice point at $t > 0$ °C is 129.2 kJ·mol^{-1}, and that for $t < 0$ °C is 27.7 kJ·mol^{-1}. The thermal conductivity at $t > 0$ °C is about 5×10^{-4} kW·m^{-1}·K^{-1}. The specific heat capacity c_p of propane hydrate exhibits the following dependence on temperature: for $t = -175$ °C, $c_p = 1.0$ J·g^{-1}·K^{-1}; for $t = -50$ °C, $c_p = 1.75$ J·g^{-1}·K^{-1}; for $t = 0$ °C, $c_p = 2.16$ J·g^{-1}·K^{-1}. The density of propane hydrate at 0 °C and equilibrium pressure is 0.866 g·cm^{-3}. Quadruple points exist at 273.1 K and 0.172 MPa[7] and at 278.3 K and 0.555 MPa.

In our experiments the subcooling of the system observed before hydrate formation onset was up to 10.7 °C. In this case the first crystals of hydrate were formed on the interface of two phases consisting of liquid propane and freshwater at (−5 to −6) °C. With the formation of hydrate at the propane + water interface, the solubility of water in liquid propane was reduced. Microdroplets of water condense in liquid propane volume. Microcrystals of hydrate were then formed on the surface of these drops of water. Accumulations of such soft crystals resemble snow in the liquid with a strongly branched surface. The subsequent retarded growth of hydrate occurs due to the diffusion of the water molecules through the hydrated film on the liquid propane + water interface to the surface of the growing crystals. In this case the rate of hydrate formation depended on the diffusion of water, which is determined by temperature.

Figures 4−7 give the characteristic curves of phase transitions during cooling and heating of the system propane + water in the region of hydrate formation. The curve ABCD in Figure 4 reflects the process of isochoric cooling of the system. Two interfaces of the phases were present in the limits of the curve CD in the system: lower, liquid propane + water; upper, liquid propane + vapor propane saturated with water vapor. Supercooling of the

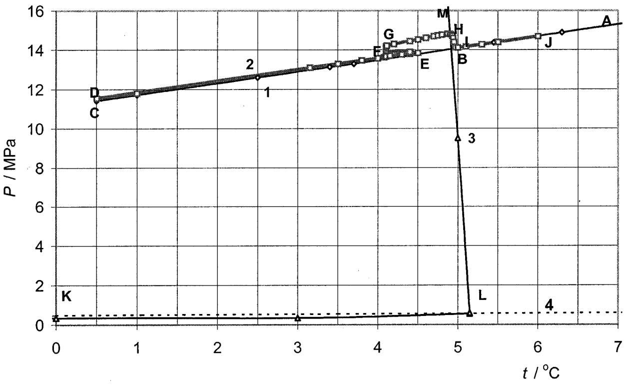

Figure 6. Propane + water hydrate formation−dissociation: 1, cooling; 2, heating; 3, equilibrium; 4, vapor pressure.

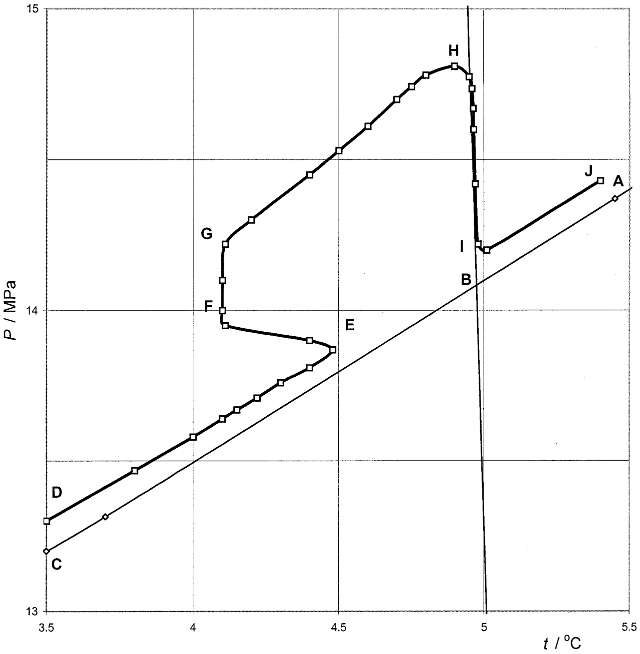

Figure 7. Fragment from Figure 6.

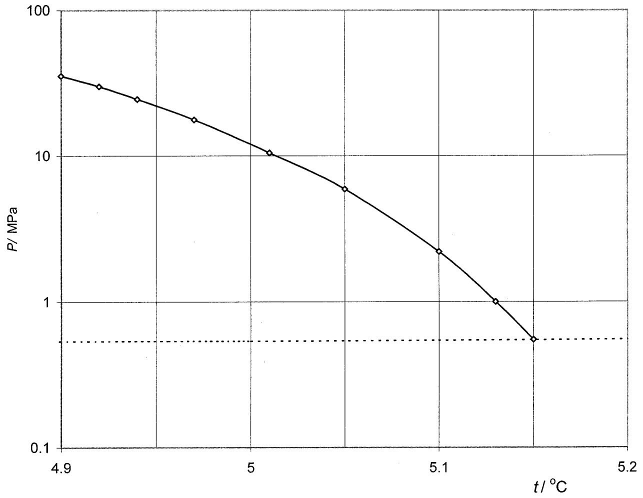

Figure 8. Equilibrium $P-t$ data for liquid propane + water hydrate: 1, equilibrium $P-t$; 2, vapor pressure.

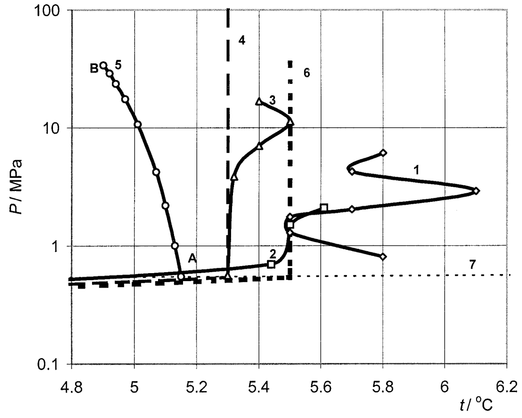

Figure 9. Liquid propane + water hydrate $P-t$ equilibrium dissociation by different authors: 1, Wilcox; 2, Reamer; 3, Verma; 4, Robinson; 5, this work; 6, Sloan; 7, propane vapor pressure.

Table 2. Equilibrium *P-t* Data for Liquid Propane + Water Hydrate

t/°C	5.15	5.13	5.10	5.05	5.01	4.97	4.94	4.92	4.90
P/MPa	0.555	1.0	2.2	5.9	10.5	17.7	24.5	30.0	35.0

system at point D was 11.1 °C; however, the process of the formation of hydrate started only after an isothermal increase in the pressure to 10.5 MPa (point E). A dense thin hydrated film was formed at the contact of the two liquid phases. Structure, density, and diffusion permeability of this film depend on the conditions of formation, pressure, temperature, composition and state of water, and so forth.

One should emphasize that the morphology and the physical parameters of a hydrate which is formed at the contact of two liquid phases and a hydrate which is formed in the volume of one of the phases are very different. With an increase in the temperature (curve EF, Figure 4) a slow diffusion growth of hydrate is observed in the volume of liquid propane. Formed hydrate presents the piling up of friable crystals with the strongly developed surface. With an increase in the temperature, the diffusion permeability of the hydrated interfacial film gradually rises, and at point F, the capillary influx of water through the pores of the hydrated film probably is manifested. In this case a sharp increase is observed in the accumulation of hydrate (curve FG). Further increase in temperature (curve GH) leads to the dissociation of hydrate (curve HI). Curve IJ is the isochoric increase in the temperature.

During the temperature maintenance at (−5 to −6) °C in the reactor, usually no ice formation is observed for many hours. However, after the formation of hydrate even an insignificant decrease in the temperature (by 0.5 °C to 1.5 °C) leads to active ice formation with an intensive increase in pressure. Figure 5 presents the characteristic curves of changes in temperature and pressure during cooling of the propane + water system with the formation of hydrate and ice. During the cooling stage, hydrate was formed at a temperature of −5 °C (point C). Further cooling of system down to −5.7 °C (point D) was accompanied by active ice formation with an increase in the pressure and temperature (curve DE), by thawing of ice and by formation of hydrate (curve EF). The structure and kinetics of formation and dissociation of hydrate, which is formed directly from the melt and condensed water, are different and require additional studies.

Figure 6 presents the curves of cooling (ABC) with the formation of hydrate (C) and heating (DJ) with the formation (DEFGH) and the decomposition (HI) of the hydrate. Figure 7 shows in greater detail the fragment of the phase transitions within the limits of temperature from (3.5 to 5.5) °C. With an increase in temperature, the structural transition of hydrate occurred at point E with absorption of heat and an increase in the volume of the hydrate (section EFG). Curve HI corresponds to the conditions of expanding hydrate. Curve IJ represents isochoric heating of the system propane + water. Figure 8 and Table 2 present the equilibrium dissociation curve (AB) of liquid propane hydrate, obtained by us on the basis of the generalization of experimental data.

Figure 9 also presents data measured by other authors.

Conclusion

Accurate data are presented for the phase transitions of the system liquid propane + water in the region of hydrate formation. Hydrates of gases with a high critical temperature, which can be condensed in the region of hydrate formation, require an additional study for the conditions of formation of hydrate from condensed water and from meltwater. Hydrate is formed before ice for the conditions of liquid propane at temperatures below the freezing temperature of water. Supercooling of (11 to 12) °C is observed before the onset of hydrate formation from liquid propane. Liquid propane hydrate formation and dissociation from condensed water and ice melting water is different and requires more study. The equilibrium curve of hydrate of liquid propane has an inclination to the left at pressures up to 35 MPa (this work) and up to 145 MPa.[8]

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