Hydrates in Systems Containing Methane, Ethylene, Propylene, and Water

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The initial hydrate forming conditions for the systems ethylene-water and methane-ethylene-water were investigated to about 9,000 lb./sq.in.abs. It was found that at a given pressure the initial hydrate forming temperature for mixtures containing greater than about 65 mole % ethylene was higher than the initial formation temperature for either methane or ethylene. Solid-vapor equilibrium ratios were calculated for the ethylene hydrate. A comparison between experimental and predicted hydrate forming conditions for the system methane-ethylene-propylene-water was made for several different mixtures of these gases. This comparison showed that the predicted hydrate forming temperature was slightly higher than the experimental at a given pressure.

The significance of gas hydrates in industry was first realized by Hammerschmidt (*5*) in 1934 when he found that the plugging of valves and pipes was due to the formation of light paraffin hydrocarbon hydrates. It has since been established that hydrates will form with a number of gases and in combination with mixtures of gases. The ratio of the number of molecules of water associated with the gas in the hydrate crystal varies with the gas or the gas mixture. Claussen (*2*), using an X-ray technique, has determined this ratio for a number of gases. He found that the value for the ethylene hydrate was 7.4.

The results of an experimental investigation of hydrate equilibria in the methane-propylene-water system have recently been described (*9*). As a continuation of this work hydrate forming conditions in the ethylene-water, methane-ethylene-water, and methane-ethylene-propylene-water system have been studied.

PREVIOUS WORK

Several workers have determined heterogeneous phase equilibrium data for the ethylene-water system. Villard (*10*) in 1888 reported experimental data for the three phase equilibrium hydrate—vapor—water-rich liquid at temperatures from 32° to 63°F. and pressures from 95.5 to 86.7 lb./sq. in. abs. By extrapolating his data Villard reported a critical decomposition temperature of 65.8°F. for this system. Diepen and Scheffer (*4*) reported data for the three phase equilibrium hydrate—vapor—ice, and the hydrate—vapor—water-rich liquid equilibrium up to 743 lb./sq. in. abs. They also reported data for the metastable equilibrium hydrate—vapor—hydrocarbon-rich liquid. Reamer, Selleck, and Sage (*8*) investigated this system up to 513 lb./sq. in. abs., but their data are scattered and do not agree well with the data of Villard and Diepen and Scheffer.

Ethylene is above its vapor-liquid critical point at the temperatures and pressures under consideration. Accordingly only the single hydrocarbon phase will exist, and there will be no region of two immiscible liquids. For this reason the methane-ethylene-water system will differ from the methane propylene-water system in that a quadruple locus corresponding to the hydrate—vapor—water-rich liquid—hydrocarbon-rich liquid equilibrium does not exist.

EXPERIMENTAL METHOD AND TECHNIQUE

The experimental technique and the experimental apparatus used in this work have been described previously (*9*), except for changes in the equilibrium cell and the method of making connections for rotating the cell under pressure. For the pressure range from 2,000 to 4,000 lb./sq. in. abs. a liquid level gauge with an approximate volume of 95 cc. was used. Windows at the front and back of the cell permitted visual observation of the cell contents. A liquid-level gauge with a volume of 300 cc. was used in the pressure range of 5,000 to 10,000 lb./sq. in. abs. This cell had a window on the front only, and therefore it was more difficult to observe the hydrate decomposition point than it was with the other two cells. To overcome this a polished stainless steel mirror was suspended inside the cell, and a narrow beam of light was directed at the crystal of hydrate under observation. The stainless steel strip reflected enough light to permit satisfactory observation of the hydrate decomposition point.

The stainless steel coils which had been used to permit agitation of the cell contents in the work with propylene were replaced in the new cells by a rotary seal. This was fabricated from stainless steel tubing inserted into a fixed steel block and sealed with teflon O-rings. The assembly worked well in service and greatly facilitated the mounting of the cell and its surrounding constant temperature bath.

The methane and propylene used had purities of 99.8 and 99.7 mole %, respectively. The ethylene had a purity of 99.5 mole %.

EXPERIMENTAL RESULTS

Methane-Water and Ethylene-Water Systems

Initial hydrate forming conditions in the hydrate—vapor—water-rich liquid

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region were obtained for methane up to about 5,000 lb./sq. in. abs. The experimental data are shown in Figure 1. The purpose of these tests was basically to verify the experimental technique because data for this system had previously been obtained by other workers (*3, 6, 10*).

This same equilibrium was studied for the ethylene-water system up to 8,629 lb./sq. in. abs. The experimental data are plotted on Figure 1 together with the previously published data of Diepen and Scheffer.

The results of this work show that the slope of the pressure-temperature locus representing the hydrate—vapor—water-rich liquid equilibrium begins to increase very rapidly at approximately 700 lb./sq. in. abs. and 62.9°F. This slope reaches a maximum at approximately 1,100 lb./sq. in. abs. and 64.9°F. Above this pressure it begins a gradual decrease but finally becomes uniform for all conditions studied above about 2,500 lb./sq. in. abs. and 69.7°F.

Methane-Ethylene-Water System

The pressures and temperatures where hydrate just begins to form were determined for mixtures of methane and ethylene up to approximately 9,000 lb./sq. in. abs. The experimental data are plotted on Figure 1 together with the hydrate forming conditions for pure methane and ethylene.

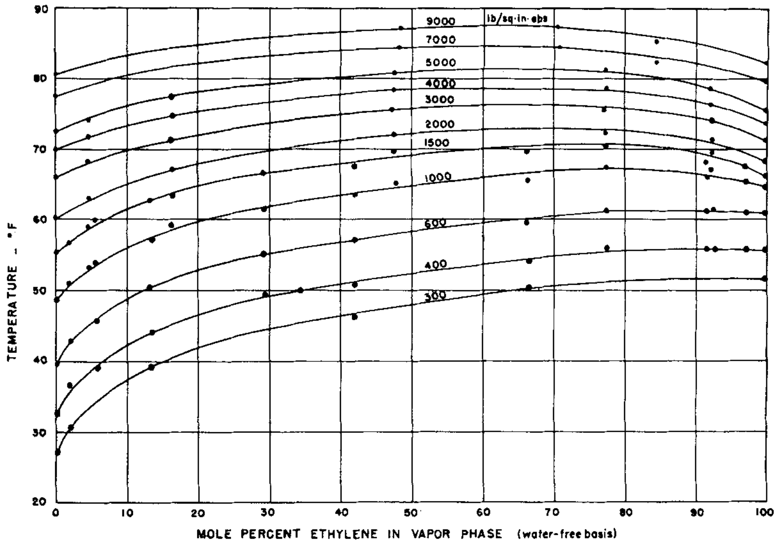

Fig. 2. Influence of composition on hydrate forming conditions in systems containing methane and ethylene.

The composition of the vapor phase, on a water-free basis, was determined at each equilibrium point. Curves were drawn through equilibrium points having approximately the same vapor composition and are shown for different mixtures ranging from 1.9 to 92.4 mole % ethylene. Below about 730 lb./sq. in. abs. the equilibrium curves for all compositions greater than about 70 mole % ethylene become indistinguishable from the curves for pure ethylene.

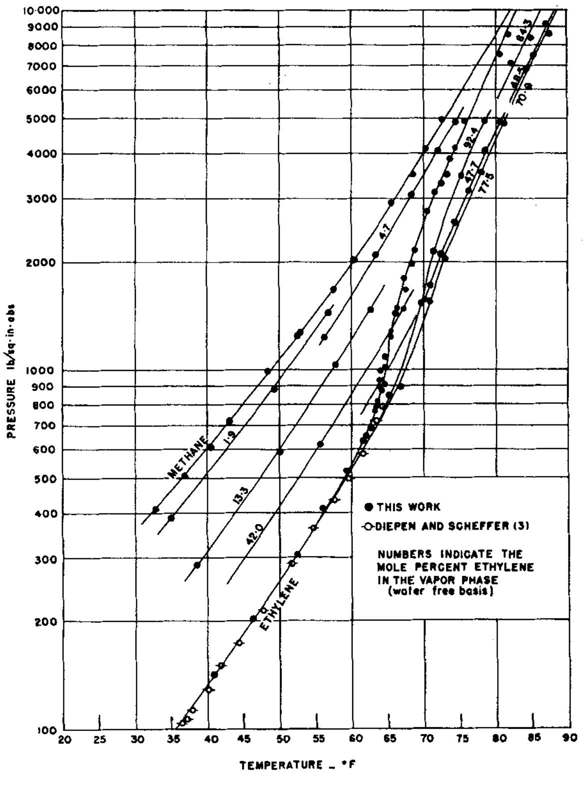

Fig. 1. Initial hydrate forming conditions in systems containing methane, ethylene, and water.

As described previously the slope of the 100% ethylene equilibrium curve becomes much greater at approximately 700 lb./sq. in. abs. The 42.0 mole % curve parallels this curve up to 700 lb./sq. in. abs. but does not suddenly increase in slope. It continues as a smooth curve with gradually increasing slope and crosses the 100% curve to give an equilibrium temperature of 70°F. at 2,000 lb./sq. in. abs. The equilibrium curve for 47.7 mole % ethylene also crosses the 100% ethylene curve. Hydrate equilibrium curves were determined for mixtures containing 92.4 and 84.3 mole % ethylene at pressures greater than 730 lb./sq. in. abs. in the former case and for pressure exceeding 5,000 lb./sq. in. abs. for the latter. Equilibrium pressures for these mixtures are lower than for 100% ethylene but are higher than that for the 47.7% mixture. For the higher concentrations of ethylene the slope of the curves first increased and then decreased again, similar to the curve for the ethylene-water system. The trend of these equilibrium curves can be more clearly seen on Figure 2 which is a cross plot drawn from Figure 1 and shows constant equilibrium pressure curves on a temperature composition diagram. The points shown on Figure 2 were obtained from smooth curves drawn through the experimental data at each of the indicated compositions. For the sake of clarity the data for only ten of the sixteen mixtures studied were reported on Figure 1.

For pressures below about 700 lb./sq. in. abs. the equilibrium temperature increases as the mole percent of ethylene increases. The slope of these pressure curves decreases as the mole percent ethylene increases. As the mole percent ethylene increases in the mixture at pressures above about 700 lb./sq. in. abs. the hydrate forming temperature passes through a maximum at each pressure. Thus it is seen that for each pressure there is a maximum temperature corresponding to a particular composition above which hydrate will not form. The locus of these maximum hydrate forming conditions is defined by the curve representing the vapor, water-rich liquid and hydrate equilibrium in the ethylene-water system for pressures up to 700 lb./sq. in. abs. At higher pressures it is approximately defined by a smooth extrapolation of this curve.

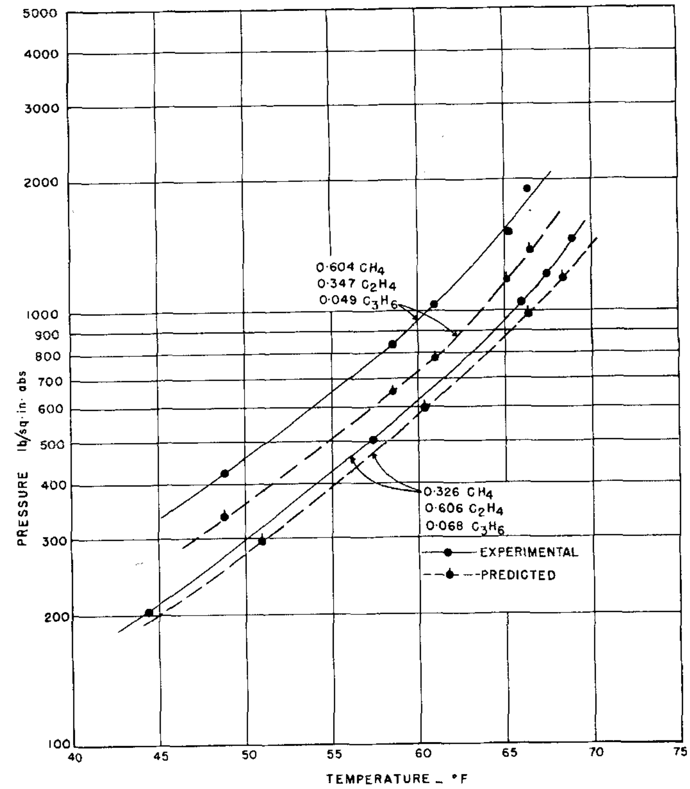

Fig. 4. Experimental and predicted hydrate forming conditions in systems containing methane, ethylene, and propylene.

EQUILIBRIUM RATIOS

Smoothed curves representing calculated equilibrium ratios for ethylene obtained from data on hydrates in the methane-ethylene-water system are shown on Figure 3. The solid-vapor equilibrium ratio is defined as $K_{v-s} = y/x$, where y is the mole fraction of hydrocarbon in the vapor and x is the mole fraction of hydrocarbon in the hydrate, both on a water-free basis. The procedure outlined by Carson and Katz (*1*) and their equilibrium ratios for methane were used for the calculations of the solid-vapor equilibrium ratios for ethylene.

The constant pressure curves for the solid-vapor equilibrium ratios for ethylene have a gradually decreasing slope until a value for K_{v-s} of approximately 0.8 is reached. The slope then increases quite sharply. This occurs because methane-ethylene mixtures containing greater than 70% ethylene form hydrates at essentially the same conditions as for pure ethylene. The equilibrium ratios are equal to unity at the pressures and temperatures at which pure ethylene form hydrates. The curves for 1,000 lb./sq. in. abs. and higher exhibit a temperature maximum above values of K_{v-s} equal to 0.9 because of the nonuniformity of the configuration of the constant composition equilibria curves in the region above 700 lb./sq. in. abs. and 62.9°F.

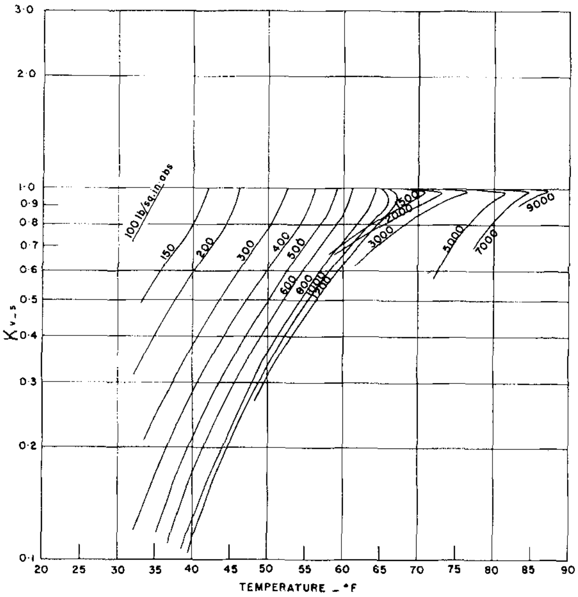

Fig. 3. Vapor-solid equilibrium ratios for ethylene obtained from hydrates in the methane-ethylene-water system.

In order to evaluate the usefulness of the calculated solid-vapor equilibrium ratios for ethylene and propylene initial hydrate forming conditions in the hydrate—vapor—water-rich liquid region were experimentally determined for several mixtures of methane, ethylene, and propylene. The procedure was to prepare gas mixtures with the three components in varying proportions and to experimentally determine the pressure and temperature where hydrates began to form. These results were then compared with the pressures and temperatures predicted for the same composition. In the predictions the equilibrium ratios calculated above were used for ethylene, those reported by Otto and Robinson (*9*) were used for propylene, and those reported by Carson and Katz (*1*) were used for methane. The calculations are made in a manner exactly analogous to a standard dew-point determination, where a pressure is selected and temperatures are chosen until $\Sigma Y/K_{v-s} = 1$. The mixtures investigated had methane concentrations ranging from 32.6 to 64.8 mole %, ethylene from 31.7 to 60.6 mole %, and propylene from 3.5 to 6.8 mole %.

Two of these comparisons are shown in Figure 4. It was found that as the percent methane in the mixture increased, the percent deviation increased. The discrepancy between predicted and experimental values indicates that predictions based on these solid-vapor ratios can only be used as a first approximation. In mixtures of hydrates containing olefinic hydrocarbons the equilibrium ratios for the individual components are evidently a function of composition. This can only be established quantitatively by analysis of hydrates formed from a vapor of fixed composition.

DISCUSSION

Experimental data for the ethylene-water system show that the pressure-temperature gradient of the curve representing the hydrate—vapor—water-rich liquid equilibrium in this system passes through two points of inflection between pressures of about 700 and 1,100 lb./sq. in. abs. The reason for this is not clear. It is known that the number of molecules of water associated with each molecule of gas in the hydrate lattice is different for different systems. It is also known that a change in crystal structure is associated with a change in slope of the vapor-pressure curve. It is suggested that the points of inflection observed for this system result from a change in the number of water molecules associated with the hydrocarbon molecule causing a change in the crystal structure of the hydrate.

In methane-ethylene-water systems containing higher concentrations of ethylene the appearance of two inflections similar to those for the ethylene-water system is observed. At lower concentrations the curves are similar and essentially parallel to the curve for the methane-water system. This is to be expected because each of these curves is a locus of points at fixed composition on a surface in space connecting the pure component curves. The folding of this surface appears to be such that at pressures above about 12,000 lb./sq. in. abs. ethylene hydrates will form at temperatures lower than for methane hydrates.

An interesting aspect of the configuration of this surface is that constant-pressure sections show a maximum temperature such that hydrates in the mixture of hydrocarbons form at a temperature above that for either single component. To the best of the authors' knowledge the hydrogen sulfide-propane system is the only other system known to exhibit this behavior (*7*).

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Taylor Instability of an Evaporating Plane Interface

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A new mode of high-flux heat transfer is proposed, which consists of film boiling from a porous solid plate, the vapor being sucked off through the plate. For horizontal plates the average vapor film thickness is determined by Taylor instability of the vapor-liquid interface. A theory is presented for predicting the minimum vapor film thickness which takes into account the stabilizing influence of the reactive pressure of the vapor leaving the interface. The predicted heat transfer coefficients are five to ten times greater than observed heat transfer coefficients in film boiling from nonporous surfaces.

Sir Geoffrey Taylor first called attention to the instability which results when an interface between two fluid phases of unequal density is accelerated away from the lighter phase (*1*). This is exactly equivalent to the instability of the interface between a dense fluid lying over a lighter fluid. Such a condition exists in film boiling of a liquid from a horizontal flat plate, where a quasistable film of vapor separates the liquid from the plate. The zone is stabilized by the presence of the hot surface which results in evaporation from the interface. Previous treatments have considered the modifying effects on Taylor instability of surface tension (*2*), viscosity (*2*), finite depth of fluids (*3*), and velocity of the fluids parallel to the interface (combined Taylor and Helmholtz instability) (*3*);