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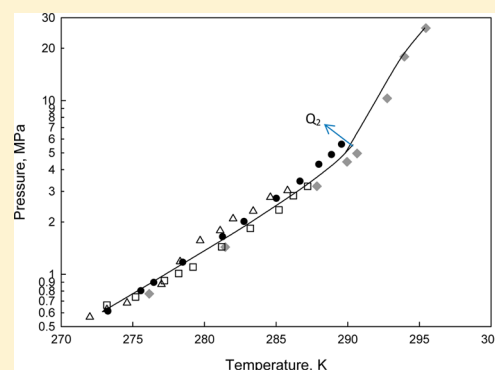
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ABSTRACT: Ethene, ethyne, and propene are common and important industrial gases which are known to form hydrates. There exists in the open literature some hydrate dissociation data for simple hydrates of the three hydrocarbons. Unfortunately the data reported in literature are in some instances very limited, and the data sets are not always in agreement with each other. To evaluate the hydrate data for these hydrocarbons, new hydrate dissociation data were measured and are compared to that in the literature. Measurements for ethyne were undertaken in the temperature and pressure ranges of (273.2 to 285.5) K and (0.614 to 2.467) MPa, respectively. The temperature and pressure ranges for the propene measurements were (273.5 to 274.4) K and (0.492 to 0.613) MPa, respectively. The solid solution theory of van der Waals and Platteeuw, together with the Valderama–Patel–Teja equation of state and the non-density-dependent mixing rules were used to model the experimental hydrate dissociation conditions. Model predictions were found to be in satisfactory agreement with the newly reported data, as well as independent measurements for the ethyne + water and ethene + water systems. However, only a fair agreement is observed when the modeled data is compared to propene hydrate dissociation data found in the literature.



1. INTRODUCTION

Gas hydrates or clathrate hydrates are ice-like crystalline compounds comprising water and small molecules, in which the latter occupy voids in the cage-like water structure.¹ Owing to their small size and ability to interact with water via van der Waals forces, ethene, ethyne, and propene are hydrate formers.¹

Ethene and propene are gases of significant industrial importance. They are the chemical building blocks for the synthesis of a wide range of products such as polyethylene, polypropylene, ethylbenzene, ethene dichloride, acrylonitrile, isopropyl alcohol, styrene, oxoalcohols, bromo-alkenes, footwear, adhesives, synthetic rubber, motor oil viscosity improvers, flavours, fragrances, film, etc.^{2–4}

Ethyne has been surpassed by olefins such as ethene and propene as the most important starting material for modern industrial chemistry. However, it is still used in the manufacturing of some chemicals as well as in metal working.⁵

The anticipation of exploiting gas hydrate formation in some processes such as gas storage, gas transportation, and separation has prompted researchers to undertake phase equilibrium measurements under hydrate forming conditions for the three gases.^{6–13}

Ethene, ethyne, and propene have boiling points which are very close to each other. As a result it is impractical and financially nonviable to use conventional methods such as

distillation, gaseous diffusion using membranes, or pressure swing adsorption to effect separation of these compounds. Gas hydrates however could provide a possible solution for these types of separations.¹⁴ By having knowledge of the varying conditions at which each component forms hydrates, a process may be developed for separation of the components.

To simulate or design such a hydrate-based process, accurate thermodynamic equilibrium data for pure and mixed gas hydrates, as well as thermodynamic models capable of describing the hydrate phase behavior are required.

Table 1 presents information on hydrate dissociation data which is currently available in the open literature. There are a number of data sets available for ethene, some of which were reported only a few months ago. Data for propene and ethyne are not as extensive as for ethene. In fact for ethyne there is only one data set that has been published. This single data set was measured more than five decades ago.¹³ Moreover, the various hydrate dissociation data for propene are not consistent with each other. To assess the data, especially for propene and ethyne, new measurements are presented in this study.

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Table 1. Literature Data for Ethene, Propene and Ethyne Hydrate Dissociation Conditions^a

guest gas	ref	$T_{\text{range}}/\text{K}$	$P_{\text{range}}/\text{MPa}$	N
ethene	6	272.0 to 285.8	0.567 to 3.035	11
	7	278.1 to 286.3	1.000 to 2.800	4
	8	279.5 to 328.0	1.170 to 465.0	46
	9	273.7 to 287.2	0.665 to 3.210	10
	10	276.2 to 295.5	0.772 to 26.131	8
	11	273.3 to 289.6	0.609 to 5.559	11
propene	6	273.7 to 274.3	0.516 to 0.610	3
	12	273.0 to 274.1	0.457 to 0.591	13
	10	270.7 to 274.2	0.432 to 0.610	15
ethyne	13	273.2 to 285.2	0.598 to 2.279	4

^a T_{range} , P_{range} and N , respectively, refer to the temperature range, the pressure range and the number of data points.

A survey of the literature revealed the absence of thermodynamic modeling in most of the previous studies on ethene, propene, and ethyne hydrate dissociation conditions. One benefit of data correlation is the possibility of describing the phase behavior under conditions that are different from those prevailing during experiments. Chapoy and co-workers¹⁰ combined the solid solution theory of van der Waals and Platteeuw along with the Cubic-Plus-Association equation of state (CPA-EoS) or the Valderama–Patel–Teja (VPT) equation of state with the NDD mixing rules to model ethene and propene hydrate dissociation conditions. Nonetheless, it was observed that no attempt was made in the literature to model dissociation data for ethyne hydrates.

In the present study, new data sets for hydrate dissociation conditions are presented for propene and ethyne. Data for ethyne were generated in the temperature and pressure ranges of (273.2 to 285.5) K and (0.614 to 2.467) MPa, respectively. For propene the temperature and pressure ranges are (273.5 to 274.4) K and (0.492 to 0.613) MPa, respectively. A modeling approach similar to that developed in a recent publication¹⁰ was used for the recently reported ethene dissociation data and new propene and ethyne hydrate dissociation data.

2. EXPERIMENTAL SECTION

2.1. Materials and Apparatus. The purity and the name of the suppliers of chemical components, viz. water, ethene, ethyne, and propene used in this study are provided in Table 2. The critical parameters and acentric factors for components used in this work are given in Table 3.

Table 2. Purities and Suppliers of the Chemicals^a

gas	origin	mole fraction purity
ethene	Afrox	0.999
propene	Afrox	0.995
ethyne	Afrox	0.999

^aUltrapure Millipore Q water was used in all experiments.

A detailed description of the experimental setup is available in the literature.^{11,15} It consists of a stainless-steel cylindrical vessel, with a volume of approximately 60 cm³, that can withstand pressures up to 20 MPa. It is immersed in a temperature-controlled ethene glycol bath. The contents of the vessel are agitated by means of a magnetic stirrer coupled to a horseshoe magnet which is driven by a small electric motor.

Table 3. Critical Parameters and Acentric Factors for Components³⁴ Used in This Work^a

component	T_C/K	P_C/MPa	ω	Z_C
ethene	282.34	5.041	0.0862	0.281
propene	364.85	4.600	0.1376	0.281
ethyne	308.3	6.138	0.1912	0.268

^a T_C , critical temperature; P_C , critical pressure; ω : acentric factor; Z_C , critical compressibility factor.

Rare earth magnets are used to ensure a strong magnetic field and thus an effective stirring.

Two platinum resistance thermometers (Pt-100s) are used to measure temperatures and check for temperature differentials between the top and the bottom of the equilibrium cell. The calculated uncertainty in the temperature measurement is estimated to be ± 0.1 K. Calibration of the temperature sensors is performed against a reference platinum resistance thermometer (WIKA digital thermometer calibration standard, model no. CTH 6500). The pressure in the vessel is measured with a WIKA pressure transducer rated for pressures up to 20 MPa. The combined expanded uncertainty on the pressure measurement is estimated to be ± 0.007 MPa. The transducer was calibrated against a pressure calibration standard (WIKA 6000).

2.2. Experimental Procedure. The well-established isochoric pressure search method was used to measure dissociation conditions for the hydrates.^{15,16} The cell which is immersed in a temperature-controlled ethene glycol bath is evacuated to 0.8 kPa for approximately 2 h. Approximately 40 cm³ of water is loaded into the equilibrium cell prior to gas being fed from cylinders through a pressure-regulating valve. The contents of the equilibrium cell are then properly mixed via agitation to ensure fairly rapid equilibrium conditions. The system is brought to the desired starting pressure and the bath temperature is set well below the hydrate formation region. When a stable pressure is observed, the temperature is decreased in order to form the hydrate. Hydrate formation in the cell is detected by a significant pressure drop. The system temperature is then increased in steps of 0.5 K in order to approach the hydrate dissociate point. Close to the dissociation point, the stepwise increase in temperature is reduced to 0.1 K. At each step, the temperature is kept constant for a sufficient time so as to reach equilibrium. In this manner, a pressure–temperature diagram is generated for each experimental run. While the system is in the hydrate stability region, an increase of temperature causes hydrate crystals to partially dissociate, thereby substantially increasing the pressure. Outside the hydrate-forming region, only a small increase in the pressure is observed as a result of temperature increase of the fluids in the equilibrium cell. A sharp change of the slope of the pressure–temperature data plot corresponds to the point at which all hydrate crystals have dissociated. This point is reported as the dissociation point in terms of the pressure–temperature combination. The combined expanded uncertainty in the temperature and pressure measurements are ± 0.1 K and ± 0.05 MPa, respectively. More details about the experimental procedure are provided in the literature.^{11,15,16}

3. RESULTS AND DISCUSSION

Experimental data for ethene, ethyne, and propene hydrate dissociation conditions are reported in Table 4. Data for ethyne and propene were measured in this study, whereas ethene

Table 4. Experimental (T_{exp}) and Calculated (T_{cal}) Dissociation Temperatures at Various Pressures (P)^a for Ethene, Propene, and Ethyne Hydrates

ethene hydrate ^d					propene hydrate					ethyne hydrate				
P/MPa	T_{exp}/K	T_{cal}/K	ARD/% ^b	AD ^c	P/MPa	T_{exp}/K	T_{cal}/K	ARD/% ^b	AD ^c	P/MPa	T_{exp}/K	T_{cal}/K	ARD/% ^b	AD ^c
0.609	273.3	272.9	0.15	0.4	0.492	273.5	273.5	0	0	0.614	273.2	272.9	0.11	0.3
0.798	275.6	275.3	0.11	0.3	0.505	273.6	273.6	0	0	0.780	275.5	275.2	0.11	0.3
0.891	276.5	276.3	0.07	0.2	0.521	273.7	273.7	0	0	0.986	277.6	277.4	0.07	0.2
1.164	278.5	278.6	0.04	0.1	0.530	273.8	273.8	0	0	1.224	279.5	279.4	0.04	0.1
1.634	281.3	281.6	0.11	0.3	0.565	274.1	274.1	0	0	1.554	281.7	281.6	0.04	0.1
1.998	282.8	283.3	0.18	0.5	0.588	274.2	274.2	0	0	1.968	283.6	283.7	0.04	0.1
2.715	285.1	285.7	0.21	0.6	0.613 ^c	274.4	274.4	0	0	2.223	284.5	284.8	0.11	0.3
3.405	286.7	287.4	0.24	0.7						2.467	285.5	285.7	0.07	0.2
4.265	288.0	288.9	0.31	0.9										
4.853	288.9	289.7	0.28	0.8										
5.559	289.6	290.4	0.28	0.8										

^aCombined expanded uncertainties U_c are $U_c(T_{\text{exp}}) = \pm 0.1 \text{ K}$, $U_c(P) = \pm 0.07 \text{ MPa}$. The reported uncertainties are based on combined standard uncertainties multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95 %. ^bARD % = $(|T_{\text{exp}} - T_{\text{cal}}|/T_{\text{exp}}) \cdot 100$, absolute relative deviation. ^cUpper quadruple point (H–L_w–L_{HC}–V). ^dFrom ref 11. ^eAbsolute deviation = $|T_{\text{exp}} - T_{\text{cal}}|$.

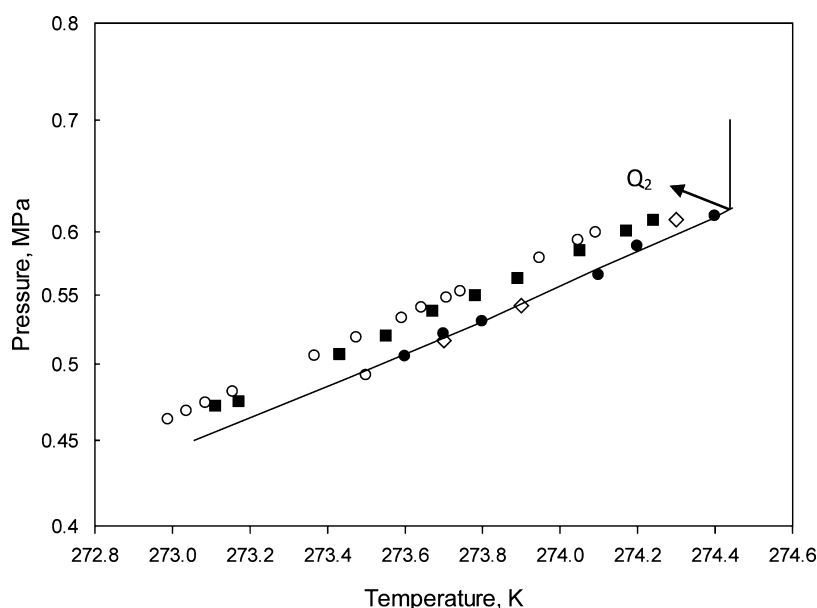


Figure 1. Experimental propene hydrate dissociation data and comparison with literature data: ●, this work; ■, ref 10; ○, ref 12; ◇, ref 6; Q₂, upper quadruple point (H–L_w–L_{HC}–V); solid line, model prediction assuming structure II; % AARD = 0.008 %. AARD = $(100/N_p) \sum_{k=1}^{N_p} |(T_{\text{exp}} - T_{\text{cal}})/T_{\text{exp}}|$.

hydrate dissociation conditions were recently published by our group.¹¹ The three sets of data were used to develop the thermodynamic model used in the present study. Table 4 also presents a comparison between the experimental data and model predictions in terms of absolute relative deviations (ARD). The developed model is based on the equality of fugacity for each component in all coexisting phases as equilibrium criterion.¹ The solid solution theory of van der Waals and Platteeuw was used for the calculation of the fugacity of water in the hydrate phase.¹⁷ Langmuir constants were calculated through the Kihara potential function.^{1,18–22} The Valderrama–Patel–Teja equation of state (VPT–EoS)²³ was used along with the non-density dependent mixing rules (NDD)²⁴ to predict the fugacity of water and that of hydrate formers in the liquid and vapor phases.

Figures 1 to 3 show plots comparing the model data to experimental data, as well as a comparison between data measured in this study and that available in literature. As far as

ethene hydrates are concerned, the discrepancy between phase equilibrium data reported in the literature has been discussed in a previous study.¹¹

The newly reported equilibrium data for propene agree with those reported by Reamer et al.⁶ However, for a given temperature, the newly reported dissociation pressures are (0.02 to 0.04) MPa lower than those presented in two other literature data sets.

As mentioned earlier, only one data set for ethyne hydrates could be found in the literature. The data measured in this study agree very well with that in literature, except at temperatures greater than 282 K.

It is fairly difficult to speculate why there are differences in dissociation data from different laboratories, and the reasons are not easily identifiable. However, the most common reasons range from purity of the chemicals used to the skill of the experimentalist, including the incorrect reporting of experimental uncertainties resulting from the calibration of pressure

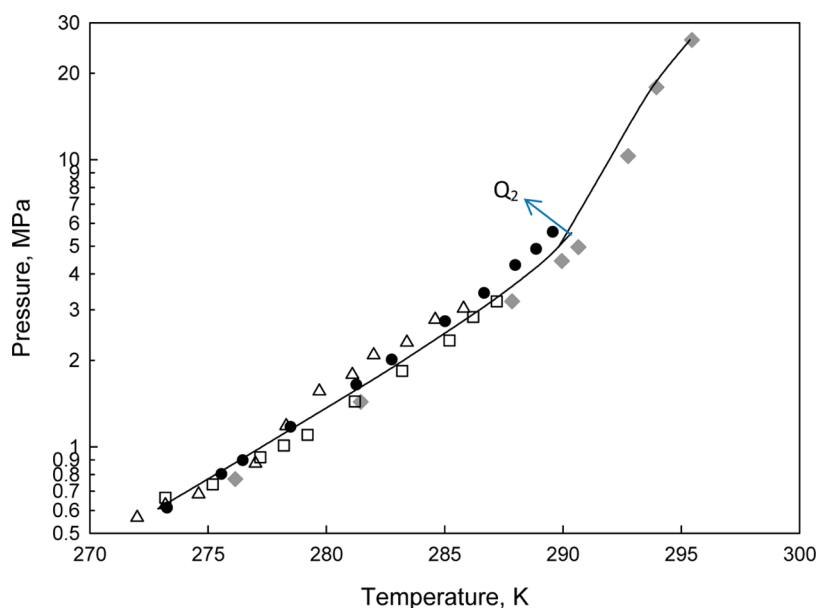


Figure 2. Experimental ethene hydrate dissociation data and comparison with model predictions: \triangle , ref 6; \square , ref 9; gray diamond, ref 10; \bullet , ref 11; Q_2 , upper quadruple point ($H-L_w-L_{HC}-V$); solid line, model prediction assuming structure I; % AARD = 0.17.

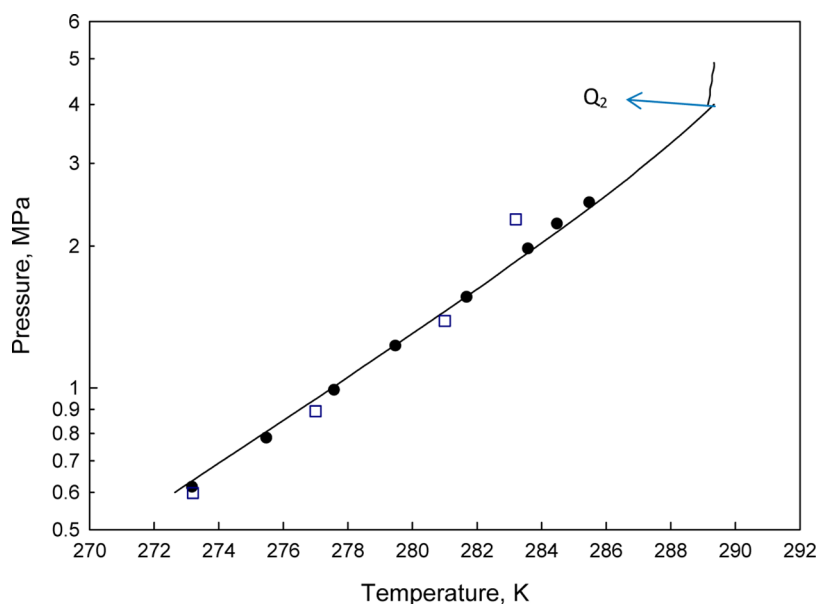


Figure 3. Experimental ethyne hydrate dissociation data and comparison with literature data: \bullet , this work; \square , ref 13; solid line, model prediction assuming structure I; Q_2 , upper quadruple point ($H-L_w-L_{HC}-V$); % AARD = 0.076.

and temperature measuring devices. For the hydrate formers under investigation, the same experimental method has been used to generate data in most of the reported hydrate equilibrium studies, viz. the isochoric pressure search method.

With regard to data correlation, binary interaction parameters (BIPs) of the VPT equation of state²³ combined with the NDD mixing rules,²⁴ i.e. k_{ij} , l_{pi}^0 and l_{pi}^1 were regressed from solubility data found in the literature,^{25–33} by minimizing the following objective function, F_{obj} :

$$F_{obj} = \left(\frac{1}{NDP} \right) \sum_{k=1}^{NDP} \left(\frac{|x_{exp} - x_{cal}|}{x_{exp}} \right)_k \quad (1)$$

where NDP is the number of data points, and x_{exp} and x_{cal} are the experimental and calculated hydrocarbon solubility in water, respectively. The BIPs are reported in Table 5.

The Kihara potential function parameters were obtained in this study for the three gases, ethene, ethyne, and propene, and

Table 5. The Optimal Binary Interaction Parameters Values between Water (i) and Hydrocarbon (j) for the VPT-EoS²³ and NDD Mixing Rules²⁴

system	k_{ij}	l_{ij}^0	l_{ij}^1
ethene (j)	0.608	1.7891	0.0031
propene (j)	0.233	0.9758	0.0030
ethyne (j)	0.226	0.9373	0.0019

are reported in Table 6 using minimization of the following objective function:

$$F_{\text{obj}} = \left(\frac{1}{\text{NDP}} \right) \sum_{k=1}^{\text{NDP}} \left(\frac{|T_{\text{exp}} - T_{\text{cal}}|}{T_{\text{exp}}} \right)_k \quad (2)$$

where T_{exp} and T_{cal} represent the experimental hydrate dissociation temperature and calculated hydrate dissociation temperature, respectively.

The Kihara potential function²¹ parameters were obtained by using the newly reported hydrate-liquid water-vapor (H–L_w–V) equilibrium data for propene and ethyne as well as data published by Tumba et al.¹¹ All the regressed parameters pertaining to both the fluid and the hydrate phases are presented in Tables 5 and 6. The phase transition parameters which were instrumental in modeling the hydrate phase are given in Table 7.

Table 6. Kihara Potential Function²⁴ Parameters Obtained in This Work

compound	$\alpha/\text{\AA}$	$\sigma/\text{\AA}$	$(\varepsilon/k)/\text{K}$
ethyne	0.3630	3.255	171.94
ethene	0.4700	3.291	172.87
propene	0.7100	3.230	203.60

Notation: α , spherical molecular core radius; σ , collision diameter; ε , characteristic energy; k , Boltzmann constant.

Table 7. Phase Transition Parameters from Water to Hydrate Used in This Work²²

$\Delta\mu_w^0/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta h_w^0/\text{J}\cdot\text{mol}^{-1}$	$\Delta\mu_w^0/\text{J}\cdot\text{mol}^{-1}$	structure
4.6	−4620.5	1297	I
5.0	−4984.5	937	II

Notation: $\Delta\mu_w^0$, chemical potential difference between empty hydrate lattice and pure water; Δh_w^0 , molar enthalpy difference between empty hydrate lattice and ice at the ice point and zero pressure; $\Delta\mu_w^0$, volume difference between empty hydrate lattice and pure water.

Results shown in Table 4, as well as in Figures 1 to 3 indicate that predictions using the suggested modeling approach are in good agreement with the newly reported data, as well as the literature data; except for propene hydrates. With regard to the data used in this study to develop the model, the average absolute relative deviations (AARD) for the predicted temperatures were calculated as 0.17 %, 0.008 %, and 0.076 % for ethene, propene, and ethyne hydrates, respectively. It was shown that the VPT EoS²³ and the NDD mixing rules²⁴ based model correlates hydrate dissociation data well for ethene and propene, as has been observed previously.¹⁰ In the present study, a similar approach to that used previously¹⁰ was undertaken. One of the differences between the two approaches lies in the method used to obtain the parameters for the hydrate phase. Furthermore, this study presents the first attempt to correlate ethyne hydrate dissociation data. The model allows the prediction of the upper quadruple point for each of the three systems investigated in this study.

4. CONCLUSIONS

New experimental dissociation data are reported for propene and ethyne hydrates. Data were measured in the temperature and pressure ranges of (273.2 to 285.5) K and (0.614 to 2.467) MPa for ethyne and (273.5 to 274.4) K and (0.492 to 0.613)

MPa for propene, respectively. The new data generally compare well with most of the literature data. A modeling approach involving the solid solution theory of van der Waals and Platteeuw,¹⁷ the VPT equation of state,²³ and the NDD mixing rules²⁴ was used to correlate the newly generated data, as well as ethene hydrate dissociation data found in the literature. A good agreement was found between the model predictions and the experimental data for ethene and ethyne hydrates. A good agreement was however observed for only one out of the three propene dissociation data sets found in the literature. The modeling approach was found to be acceptable and reliable for the three examined hydrate forming systems, that is, ethene–water, propene–water, and ethyne–water systems. The upper quadruple point for these systems is also predicted.

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Notes

The authors declare no competing financial interest.

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