

High Pressure Measurements and Molecular Modeling of the Water Content of Acid Gas Containing Mixtures

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Abstract

Water content of three carbon dioxide containing natural gas mixtures in equilibrium with an aqueous phase was measured using a dynamic saturation method. Measurements were performed up to high temperatures ($477.6\text{ K} = 400\text{ }^{\circ}\text{F}$) and pressures ($103.4\text{ MPa} = 15,000\text{ psia}$). The perturbed chain form of the statistical associating fluid theory (PC-SAFT) was applied to predict water content of pure carbon dioxide (CO_2), hydrogen sulfide (H_2S), nitrous oxide (N_2O), nitrogen (N_2) and argon (Ar) systems. The theory application was also extended to model water content of acid gas mixtures containing methane (CH_4). To model accurately the liquid-liquid equilibrium (LLE) at sub-critical conditions, cross association between CO_2 , H_2S and water was included. The agreement between the model predictions and experimental data measured in this work was found to be good up to high temperatures and pressures.

Keywords: PC-SAFT, water content, acid gas, natural gas

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Introduction

Natural gas dehydration is an essential process in any natural gas processing plant. The main goal of gas dehydration is removing water to reduce pipeline corrosion and eliminate line blockage caused by hydrate formation. The water dew point should be below the lowest pipeline temperature to prevent free water formation. Also, most product specifications require that no free water be present. As a result, the maximum water content allowed in a sales gas range between 4 to 7 lb/MMSCF. For liquids, the water content is 10 to 20 ppmv. Hydrate formation may occur not only in pipelines, but also in cryogenic processes such as the production of liquefied natural gas (LNG) and of C₂₊ raw materials needed for the polymers industry. Furthermore, enhanced oil recovery (EOR) processes related to the injection of nitrogen or acid gases have gained more attention during the last few years as an effective method of increasing oil and gas production. The process depends on compressing acid gases exiting the amine regenerator overhead or nitrogen exiting the nitrogen rejection unit and transporting them via pipelines to an injection well^{1,2}. Consequently, designing both natural gas dehydration and acid gas injection schemes requires a detailed knowledge of wet and sour natural gas mixtures. Experimental data for water content of n-alkanes are widely scattered while that for acid gases is limited. Therefore, rigorous thermodynamic models are needed to accurately predict water content at conditions where experimental data is scattered or does not exist.

Previous experimental efforts in measuring water content of acid gases

Experimental efforts in measuring water solubility in vapor carbon dioxide phase started back in 1939 by Wiebe and Gaddy³⁻⁵. Latter, Gillespie and Wilson⁶ as well as Song and Kobayashi⁷ extended the range of existing data to higher pressures where liquid carbon dioxide phase is formed below the pure CO₂ critical point. The later also provided extensive data at CO₂

supercritical conditions. In general, reasonable agreement can be observed among various sets of data above hydrate formation temperatures and up to intermediate pressure regions. Water content for CO₂ + H₂S mixtures was also measured at several conditions by Clark.⁸ Furthermore, Song and Kobayashi⁹ examined the effect of adding CO₂ on water content of methane and ethane supercritical gases. The present work will present new experimental data on the water content of 90% methane + 10% carbon dioxide, 30% methane + 70% carbon dioxide and 5% ethane + 95% carbon dioxide.

Experimental data found in the literature concerning H₂S systems is scarce. The work by Selleck et al.¹⁰ and Gillespie et al.¹¹ on water content of vapor and liquid H₂S is considered to be the most reliable in the literature. A study by Chapoy et al.¹² on the phase behavior of water-hydrogen sulfide system has provided more data at low temperatures and pressures. Furthermore, Sharma¹³ examined water content of two different CH₄+H₂S mixtures at 327.59 K (130 °F). Consequently, a fundamental equation of state is needed to safely predict water mole fractions in the absence of experimental data.

Previous modeling efforts in predicting water content of acid gases

Predicting water content in sweet and sour natural gas systems represents a great challenge to researchers as a result of the low water concentration in the hydrocarbon or acid gas phase. Therefore, most of the techniques used traditionally by the gas industry rely on charts and empirical correlations to approximate water mole fraction. At low pressures where the ideal gas approximation is valid, water content of a gas is approximated to be equal to the vapor pressure of pure water divided by the total pressure of the system. This relation assumes that the solubility of gases dissolved in water is minimal. Therefore, the mole fraction of water in the aqueous phase is taken to be unity. The assumption can be reasonable only in the presence of

hydrocarbons; however, solubility of acid gases in water can be significant even at low pressures. Sharma and Campbell¹⁴ were the first to propose a method for calculating water content of sour natural gas mixtures. The model requires the fugacity of water at saturation as well as the fugacity of water and the compressibility factor of the gas mixture at system conditions respectively. A chart was provided to estimate the fugacity at the system conditions. However, the chart is valid only for temperatures between 299.82 and 344.26 K (80-160 °F) and for pressures less than 13.79 MPa (2000 psia). Later, Maddox^{15,16} developed a similar method which relies on reading water content of sweet natural gas from the McKetta-Wehe chart and then correcting for acid gas presence using other respective charts. The chart for CO₂ is for temperatures between 299.82 and 344.26 K (80-160 °F) and the chart for H₂S is for 299.82 and 410.93 K (80-280 °F). Both charts are for pressures from 0.69-20.68 MPa (100-3000 psia). In addition, Carroll¹⁷ suggested using the Bukacek method¹⁸ instead of the McKetta-Wehe chart¹⁹ for estimating water content of the sweet gas needed for the Maddox correction method. Wichert and Wichert²⁰ proposed a correction for the McKetta-Wehe chart to take into account H₂S in the gas. The correction factor is calculated using a chart which is only valid for temperatures between 283.15 and 449.82 K (50-350 °F) and a pressure range of 1.38-68.95 MPa (200-10,000 psia). Also, the method is not applicable for H₂S equivalent mole fractions greater than 55%. It is unclear how these methods will behave if extrapolated beyond the range. The pressure and temperature limitations of most of these models are great disadvantages.

Carroll developed a more rigorous thermodynamic model (AQUAlibrium) for estimating water content of sweet and sour natural gas^{17,21,22}. The model uses the Peng-Robinson (PR) equation of state²³ to model the non-aqueous phase while modeling the water-rich phase using Saul and Wagner formulation²⁴ of the International Association for the Properties of Water and Steam

(IAPWS) equation of state for pure water. Hydrocarbon and acid gas solubility in the aqueous phase was calculated using Henry's law relations. The model was applied independently by Carroll^{17,21,22} and Yarrison et al.^{25,26} and showed superiority over other empirical correlations and charts found in the literature. Valtz et al.²⁷ used three different models to represent H₂O-CO₂ vapor-liquid equilibrium (VLE). The first model employs the PR equation of state combined with the classical van der Waals one mixing rule for modeling the vapor phase and Henry's law treatment for modeling the liquid phase. The second and third model use the PR equation of state combined with Wong-Sandler/Huron-Vidal mixing rule^{28,29} (PR + WS + NRTL) and SAFT-VR equation of state^{30,31} respectively. It is worth noting that SAFT-VR required two large binary interaction parameters to fit the experimental VLE data satisfactory. Results showed that the first and third models gave similar accuracies in predicting CO₂ mole fraction in the aqueous phase while the second model produced the best predictions in terms of water content of the CO₂ vapor phase. Furthermore, Chapoy et al.¹² used the Valderrama modification of the Patel-Teja (VPT) equation of state³² with the non-density dependent mixing rules³³ (NDD) for describing H₂O-H₂S binary system phase behavior. Again, a relatively high interaction parameter was used to correlate the experimental data in both phases. Tsivintzelis et al.^{34,35} applied the Cubic-Plus-Association (CPA) equation of state³⁶ to model H₂O-CO₂ and H₂O-H₂S binary systems. Best results were achieved when CO₂ was modeled as an electron acceptor while H₂S was modeled as an electron donor. Cross association energies were obtained from calorimetric³⁷ and infrared (IR) spectroscopic³⁸ experiments while cross association volumes were fit to experimental data. However, the work still required large positive binary interaction parameters to enhance the correlation performance.

A new water model based on the perturbed chain form of the statistical associating fluid theory³⁹⁻⁴² (PC-SAFT) was presented in our previous publications^{43,44}. Water in the hydrocarbon phase was modeled as a sphere of diameter 3Å surrounded by a sea of n-alkane chains. Calculations showed that self-association and multipolar interactions can be neglected in this phase due to the extremely low water mole fractions. Therefore, the water dispersion energy (ϵ/k) can be fitted to experimental data available in the literature⁴⁴. The pure liquid water phase was modeled using the accurate IAPWS equation of state⁴⁵. An average dispersion energy of 204.7 K turned out to be sufficient for correlating water content of the hydrocarbon phase. This value is lower than that fitted by Gross and Sadowski⁴² for their two associating sites water model (one electron donor and one electron acceptor, 2B) but is still higher than that used by water models in molecular dynamic simulation⁴⁶. The remaining association parameters for our four associating sites (two electron donors and two electron acceptors, 4C) model were then fitted to saturated liquid densities and vapor pressures of pure water. Application of the new model to predict water content of pure acid, inert and noble gases, namely: carbon dioxide (CO₂), hydrogen sulfide (H₂S), nitrous oxide (N₂O), nitrogen (N₂) and argon (Ar) as well as acid gas mixtures with methane is presented in this work.

Experimental Measurement

Experimental Set Up

The solubility of water in high temperature, high pressure hydrocarbon gases is measured using a flow scheme similar to that of Benson⁴⁷ or Rigby and Prausnitz⁴⁸. Figure 1 shows the important components of the experimental apparatus, which consists of a gas cylinder (S), a 1000 cm³ Ruska boost pump (P1), a 500 cm³ Ruska main pump (P2), a 24 foot thermal equilibration coil (EC), the saturation cell (SC), on-off and throttling valves (TV1 and TV2), analysis train and a

flow meter (F). Both EC and SC are contained in a thermostatically controlled air bath, which is controlled to within 0.3 K using a 1.8 KW heater coupled to an OMEGA CN9000A PID temperature controller. The controller parameters were determined using the Cohen-Coontz tuning method.

A detailed drawing of the saturation cell is given in Figure 2. The cell has a nominal internal volume of 1,300 cm³, with an internal diameter of approximately 7.5 cm. Gas enters the cell and flows through a glass dispersion frit (PF) which disperses the gas into the liquid water as bubbles of a nominal diameter of 0.01 mm. A stainless steel retaining ring (RR) holds the frit in place at the bottom of the cell. The bubbles travel through the liquid water phase and into the head space of the saturation cell. A stainless steel baffle and an anti-entrainment section (shown in grey) prevent any water spray from leaving the saturation cell. Gas exits the saturation cell through two throttle valves; (TV1) is a standard vee stem valve, while TV2 is a precision needle valve for precise flow control, which reduces the outlet pressure to approximately 1 bar before passing to the analytical train. Three different pressure transducers (PT) monitor cell pressure; pressures below 70 bar use a Heise transducer, pressures from 70 to 700 bar use a Data Instruments transducer, and pressures from 700 to 1400 bar use a Sensometrics transducer. A J-type thermocouple (TC) located in a thermowell (TW, shown by cross hatching) monitors cell temperature. The J-type thermocouple was calibrated by OMEGA engineering against the ice and boiling points of water, and the melting points of tin and zinc, and was checked against a NIST traceable PRT to confirm the accuracy. An Autoclave Engineers rupture disc (RD) mounted in the anti-entrainment section provides over pressure protection. The dashed line indicates the approximate water level in the cell.

Analytical train A consists of the General Electric (GE)-Panametrics moisture analyzer (PMA), three desiccant charged stainless steel u-tubes (U) and gas flow meter (F). The PMA measures the water content by measuring the resistance across an aluminum oxide sensor; as the water present in the gas stream changes, so does the resistance across the sensor, which is converted by the PMA into a mole fraction and a mass of water per volume reading. The unit is calibrated by GE using NIST traceable standards, and is recalibrated by GE yearly. Both PMA and the desiccant charged tubes are used at temperatures below 333 K but temperature limitations of the PMA prevent its use above this temperature. All tubing between the throttle valve (TV1) and analytical train is maintained 10-20 K above air bath temperature using electrical heating tape to prevent condensation. The expansion pressure inside the detector was maintained constant during a run, and generally varied between 20 and 25 psia.

A Sartorius CP-5000 series scale, with an accuracy of 0.01 mg and a maximum capacity of 300 g is used to weigh the u-tubes. The scale has an internal calibration and temperature correction features. The calibration is checked periodically against a set of standard grade Ohaus weights. More details on the experimental procedure followed in this work can be found in Yarrison²⁵.

Materials

The gas mixtures were prepared by Aeriform Gas Company, and have an uncertainty in the composition of 0.05 to 0.01 mole percent. Standard laboratory grade deionized, UV sterilized water with a maximum conductance of 0.25 micro siemens (μS) is used without further distillation. The anhydrous ACS grade magnesium perchlorate used is from VWR.

Experimental Accuracy and Precision

The experimental accuracy should be better than 5% (mole) of water content in the gaseous phase, temperatures should be within 0.5°C of set point and pressures should be within 0.01% of full scale for the high temperature apparatus.

Thermodynamic Modeling

For a water-gas binary system, the phase equilibrium can be expressed as:

$$y_{H_2O} \varphi_{H_2O}^{sat} p = (1 - x_{AG}) f_{H_2O}^{(T,p),pure} \quad (1)$$

Where y_{H_2O} is the mole fraction of water in the gas rich phase, $\varphi_{H_2O}^{sat}$ is the fugacity coefficient of water in the gas rich phase evaluated using PC-SAFT, p is the total pressure, x_{AG} is the gas mole fraction in the water rich phase, and $f_{H_2O}^{(T,p),pure}$ is the fugacity of pure liquid water evaluated at temperature T and pressure p . Using the fact that the aqueous phase is predominantly water, the activity coefficient of water is assumed to be unity.

Equating the fugacity of the gas component between the vapor and the aqueous phase gives:

$$y_{AG} \varphi_{AG}^{sat} p = x_{AG} H_{AG,H_2O}(T, p) \quad (2)$$

Where φ_{AG}^{sat} is the fugacity coefficient of the gas in the vapor phase evaluated using PC-SAFT. H_{AG,H_2O} is the Henry's law constant of the gas in the liquid water phase at temperature T and system pressure p , y_{AG} and x_{AG} are the mole fractions of the gas in the vapor and liquid phases, respectively. $H_{AG,H_2O}(T, p)$ is the Henry's law constant for the gas in water at temperature T and pressure p . Pressure and temperature dependent Henry's constant for acid/ inert gases considered in this work are calculated using the Krichevsky-Kasarnovsky equation⁴⁹

$$\ln H_{AG,H_2O}(T, p) = \ln H^{AG,0} + \frac{V_{AG,H_2O}^{\infty}}{RT} (p - p_{H_2O}^{sat}) \quad (3)$$

where $H^{AG,0}$ is the Henry's law constant for the gaseous species in water at temperature T and water saturation pressure, and V_{AG,H_2O}^∞ is the partial molar volume of the gaseous species in water at infinite dilution. $H^{AG,0}$ for CO_2 , H_2S , N_2 and Ar is calculated using a method developed by Harvey⁵⁰ while that for N_2O using the correlation by Versteeg and van Swaaij⁵¹. V_{AG,H_2O}^∞ for CO_2 , N_2O , N_2 and Ar is calculated using the corresponding states method of Lyckman et al.⁵² and for H_2S using an improved Lyckman type model developed by Yarrison^{25,26}. Detailed explanation of the model used can be found in our previous publication^{26,44}.

PC-SAFT parameters for pure water, based on the two electron donor and the two electron acceptor association scheme (also called the 4C association scheme), as well as for pure non-associating CH_4 , CO_2 , H_2S , NO_2 , N_2 and Ar components are illustrated in Table 1.

Interactions in both CO_2 -water and H_2S -water systems have been extensively studied experimentally and theoretically through *ab initio* calculations. Results indicated that the interactions between acid gases and water molecules are dominantly of a Lewis acid-base nature along with weaker hydrogen bonding interactions. Danten et al.⁵⁴ claim that the carbon atom in carbon dioxide acts as an electron acceptor while oxygen atom in water acts as an electron donor. On the other hand, quantum calculations⁵⁵⁻⁵⁷ performed by different researchers suggest that the most stable interaction existing between water and hydrogen sulfide occurs when the latter acts as an electron donor while water acts as an electron acceptor.

Following the approach taken previously by Tzivintzelis et al.^{34,35} in modeling water content of acid gases using the cubic plus association (CPA) equation of state, cross association between H_2S -water and CO_2 -water were taken into consideration, in this work, through modeling H_2S

with two negative association sites and CO₂ with two positive association sites. Self-association between H₂S molecules are known to be weak, and hence neglected. In order to reduce the number of fitting parameters, cross association energies ($\epsilon^{A_i B_j}/k$) were fixed to values determined through calorimetric³⁷ and infrared (IR) spectroscopic³⁸ experiments. The work by Tsvintzelis et al.^{34,35} required large binary interaction parameters (k_{ij}) between CO₂, H₂S and water as a second fitting parameter. On the other hand, all k_{ij} values were set to zero throughout this work. As a result, the only remaining parameter to be fit to experimental data is the cross association volume ($\kappa^{A_i B_j}$). Assuming $\kappa^{A_i B_j}$ to be temperature independent, corresponding parameters for CO₂-water and H₂S-water were fitted to single temperature water content data at 304.21 K (87.9 °F) and 366.48 K (200 °F) respectively. In this way the model predictive power in calculating water mole fractions at different conditions can be better examined. Table 2 illustrates the cross association parameters used in this work.

Results and Discussion

Measured water content of CO₂ containing natural gas mixtures

Water content of CO₂ containing natural gas mixtures are reported in Table 3 based on the approach described in the experimental setup section.

Water content of pure carbon dioxide

Vapor-liquid equilibrium (VLE) of water-carbon dioxide system was modeled using Eqs. 1-3. Experimental data by Gillespie and Wilson as well as Song and Kobayashi on the solubility of water in carbon dioxide at 304.21 K (87.9 °F) was used to fit the cross association volume ($\kappa^{A_i B_j}$) parameter as shown in Table 2. An average absolute deviation (AAD) of 7.82% was

calculated from the optimization algorithm. Figure 3 (a)-(f) exhibits results obtained at different temperatures while setting the binary interaction parameter as zero.

The model predictions appear to be in good agreement with the existing experimental data up to high temperatures and pressures. In reference to Figure 3 (a)-(d), it can be observed that water content tends to decrease up to intermediate pressures followed by a sudden jump in water mole fraction caused by CO₂ phase transition from vapor to liquid. This phenomena can no longer be observed above pure CO₂ critical point as shown in Figure 3 (e)-(f). In general, the solubility of water in CO₂ vapor phase can be captured using an inert CO₂ scheme as proposed by Gross and Sadowski⁴¹. However, once the mixture dew point pressure is reached, hydrogen bonding becomes more significant with the density increase. As a result, the sudden increase in water content can only be captured through considering cross association between CO₂ and water. The theory confirms experimental observations suggesting a weak dependence on pressure for water mole fraction in the liquid CO₂ phase.

Water content of pure hydrogen sulfide

Experimental data on water content of hydrogen sulfide is limited. Among these data points found in the literature, are smoothed values published by Selleck et al.¹⁰ based on the scattered experimental data measured by Gillespie et al.¹¹ The model cross association volume, $\kappa^{A_i B_j}$, was fitted to experimental data by Gillespie et al.¹¹ at a temperature of 366.48 K (200 °F). An average absolute deviation (AAD) of 13.8% was calculated from the optimization algorithm. The fitted value was then used to predict water solubility at different temperatures as shown in Figure 4 (a)-(e).

In reference to Figure 4 (b), the model over predicts water solubility in liquid H₂S phase at 344.26 K (160 °F) in comparison to the experimental values by Gillespie et al.¹¹ The same trend was obtained by Carroll^{17,22} using AQUAlibrium software package which uses a Peng-Robinson (PR) equation of state in modeling the non-aqueous phase. Moreover, another set of smoothed data from Selleck et al.¹⁰ does not show a three phase point at temperature of 377.59 K (220 °F), which is above pure H₂S critical point. However, the model in Figure 4 (d) predicts the existence of a three phase point which is in agreement with what has been shown previously by Carroll and Mather⁶¹. In general, the agreement between the model predictions and literature values is reasonable considering the scatter found in the original experimental data.

Water content of pure nitrogen, argon and nitrous oxide

Modeling phase behavior of water-nitrogen and water-argon binary systems is simpler than that of CO₂, H₂S and N₂O since no LLE is formed at conditions under consideration. Coan and King⁵⁸ argue that N₂O hydration occurs in the vapor phase as a result of Lewis acid-base type of interactions. Since, no LLE data is found in the literature for N₂O-water system and hydration is expected to be weak in the vapor phase, cross association between N₂O and water was neglected in this work. Moreover, parameters for N₂O were obtained through fitting pure saturated liquid densities and vapor pressures as shown in Figure 5 (a)-(b) and Table 1.

Experimental data^{48,63-70} found in the literature for nitrogen systems cover a wide range of conditions from 273-623 K (32-662 °F) and up to 135 MPa (19,580 psia). On the other hand, the only data available on water content of compressed argon⁴⁸ and nitrous oxide⁵⁸ cover a narrower range of temperature from 298.15-373.15 K (77-212 °F) and pressures up to 9.27 MPa (1345 psia) and 5.00 MPa (725 psia) respectively. Again, the k_{ij} parameters were set to zero as

followed in the case of water-alkane and water-CO₂/H₂S systems. As evident in Figures 6-8, there is good agreement between the model predictions and the experimental data.

Water content in methane-CO₂ and methane-H₂S mixtures

Natural gas streams entering a glycol dehydration unit in a gas plant is usually a mixture of light hydrocarbons, mostly composed of methane, water, small percentages of carbon dioxide and traces of hydrogen sulfide. Therefore, modeling the effect of acid gases on water content of methane is essential for industrial applications. To do so, binary mixtures of methane-carbon dioxide and methane-hydrogen sulfide needs to be first modeled using PC-SAFT. Figure 9 (a)-(b) depicts the phase behavior of methane-carbon dioxide and methane-hydrogen sulfide respectively.

Fitted binary interaction parameters along with the absolute average deviations from experiment are shown in Table 4 for methane-carbon dioxide and methane-hydrogen sulfide systems. The binary interaction parameter tabulated for carbon dioxide-hydrogen sulfide system will be used later in the next section of this work. Although adding a k_{ij} value to each of these systems has been proved to substantially reduce the error in the liquid phase, we decided to keep the model predictive and neglect them while modeling the ternary systems. Figure 10 (a)-(f) demonstrates the effect of adding CO₂ at different concentrations on the solubility of water in the methane-rich phase.

The agreement between the model predictions and the experimental values for Figure 10 (a)-(e) is satisfactory. Now, the model was used to predict water content at conditions where experimental data is absent. Figure 10 (f) shows water solubility in methane-carbon dioxide mixture as a function of pressure and composition at 298.15 K (77 °F). An increase in the

pressure from 1.38 to 5.52 MPa (200-800 psia) leads to a reduction in the solubility of water in the vapor phase. At a constant pressure, it is demonstrated that water content decreases linearly with increasing methane concentration. However, a pressure point is reached where liquid CO₂ starts forming and a jump in water content of pure CO₂ occurs. PC-SAFT calculated that dew point pressure, at 298 K (77 °F), to be about 6.24 MPa (905 psia). The sudden decrease in water content at 6.55 MPa (950 psia) is due to the phase transition from liquid to vapor once methane is added to the system. Further increase in pressure from 13.79-20.68 MPa (2000-3000 psia) resulted in an increase in the water content of the supercritical natural gas fluid. However, now water mole fraction decreases exponentially with increasing methane concentration at a constant pressure. Figure 11 (a)-(b) depicts the solubility of water in two different gas mixtures of methane-hydrogen sulfide at 327.59 K (130 °F).

As expected, the effect of H₂S composition the on water content of the methane-rich vapor phase was weak. Tables 5 and 6 compare the model performance against predictions done by Carroll²¹ using McKetta-Wehe chart, Wichert correction, AQUAlibrium software package (AQUA.) and Bukacek-Maddox method (B-M).

Although the binary interaction parameters for PC-SAFT have been set to zero, results show that PC-SAFT performs as well as Bukacek-Maddox method in predicting water content of H₂S systems and performs similar to AQUAlibrium software package in predicting water content of CO₂ systems. Better predictions for the water content of H₂S can be achieved using McKetta-Wehe chart, Wichert correction and AQUAlibrium software package. Predictions for H₂S systems using PC-SAFT might be improved by tuning the $\kappa^{A_i B_j}$.

Water content of sour natural gas mixtures

Application of the water model in modeling a typical sour natural gas mixture is important for industrial processes. Accurate determination of water content is essential for preventing hydrate formation in pipelines. Also, designing injection schemes for EOR applications require a strong understanding of the phase behavior of wet acid gas systems. PC-SAFT predictive power was examined through modeling a quaternary mixture of methane, carbon dioxide, hydrogen sulfide and water at industrial pipeline conditions. First, the ability of the equation of state in describing CO₂-H₂S binary system phase behavior was tested. In reference to Figure 12, it is interesting to observe as how adding a k_{ij} value causes a change in the shape of the binary mixture phase envelope. The fitted k_{ij} is listed in Table 4.

Second, an attempt was made to predict water content of mixed CO₂-H₂S gas mixture. Setting all k_{ij} values as zero, PC-SAFT was able to adequately predict water content of the mixture at two different compositions as shown in Figure 13 (a)-(b). Now the model can be used confidently to model the quaternary mixture at industrial conditions.

Finally, water content of two quaternary mixtures was predicted and is shown in Table 7.

Generally, the error increases with increase in system temperature and pressure. The same observation can also be seen in Figure 3 (f) at a high temperature of 477.59 K (400 °F). It is worth noting that Clark⁸ attempted to model Huang et al.⁷⁵ data using AQUAlibrium software package and performed almost equal to PC-SAFT. Although, the absolute deviations (AD) are within $\pm 30\%$ of the experimental data, setting k_{ij} values as zero might have contributed in increasing the absolute average deviations.

Conclusion

Water content of three CO₂ containing natural gas mixtures was measured up to high temperatures and pressures and as a function of carbon dioxide concentration using a dynamic saturation method. A water model developed based on water content data in n-alkanes was used to predict water content of pure acid, inert and noble gases as well as acid gas mixtures containing methane. To do so, cross association between water-CO₂ and water-H₂S was taken into account. Association energies were fixed to experimentally determined values, while association volumes were fitted to VLE and LLE data. Interaction parameters were set to zero throughout the work. The agreement between the model predictions and experimental data for pure acid, inert and noble gases was good up to high temperatures and pressures. Moreover, the effect of acid gas composition on water content of the methane rich phase was examined. Water mole fraction showed a weak dependence on acid gas composition at VLE conditions while a strong dependence was shown at supercritical conditions. Finally, an attempt was made to predict water content of a typical natural gas stream at industrial conditions. Errors were relatively high but were still within $\pm 30\%$ of the experimental data. SAFT is a general model applicable to a wide range of systems; yet the results are competitive with the best models created for the specific case of water content in acid gas systems.

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