Reliable Prediction of Aqueous Dew Points in CO_2 Pipelines and New Approaches for Control During Shut-in

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ABSTRACT

Accurate predictions and precise control of the allowable water content in CO_2-rich fluids are required in large-scale pipeline operations. Especially during transient shut-in and re-start operations, the pressure decrease associated with cooling may cause the CO_2-rich mixture to pass through its dew point, producing an aqueous liquid phase. The pH of this liquid aqueous phase will rapidly decrease as carbonic acid is formed, greatly accelerating the corrosion rate of the carbon steel pipeline. The phase behaviour of CO_2-rich fluid mixtures is qualitatively different to that of hydrocarbons, and standard oil and gas property packages in process simulation software may be inadequate for predicting dew points and other key properties. An extensive literature survey reveals 37 data sets where water contents of CO_2-rich fluids have been measured near conditions relevant to CO_2 pipelines. Following consistency tests, 26 data sets were found to be of good quality and 11 data sets were found to be of poor quality. The good-quality data were compared with predictions from 6 equations of state. Overall, Multiflash's RKS (Advanced) model was found to provide the best agreement with the aqueous dew point data of CO_2-rich fluid phases. A case study is presented wherein it is demonstrated that the formation of a corrosive aqueous phase can be avoided during shut-in via introduction of a relatively small volume of ethanol.

Keywords

CO_2 pipelines
CO_2 specification
Dew point control
Corrosion

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Introduction

Sequestration of produced carbon dioxide (CO_2) is an increasingly important consideration in the development of new oil and gas production facilities. The removal of CO_2 from natural gas is typically achieved via an amine contact process. The resultant wet CO_2 stream is dried, compressed, and transported via pipeline for injection. Under normal operating conditions the CO_2-rich fluid is expected to maintain high temperature and pressure throughout the pipeline. However, under transient shut-in and re-start operations, fluid conditions may differ substantially from those of normal operation. If excess water is present, changes to the fluid condition may result in the mixture's dew point being crossed, resulting in the formation of a corrosive aqueous phase that could damage the pipeline. Preventing this from occurring is essential for the continued safe use of the pipeline. Hence, predicting reliably dew point conditions of CO_2-rich fluids is of substantial importance, particularly in the presence of likely impurities.

In the DNV's 'Recommended Practice: Design and Operation of CO_2 Pipelines' (DNV, 2010), it is suggested that the mass density of overwhelmingly pure CO_2 streams can be satisfactorily obtained with the Peng Robinson equation of state (Peng and Robinson, 1976). However, the important issue of predicting H_2O solubility in the fluid is barely addressed: the DNV recommendation is that designers and operators should tune their models to appropriate experimental data relevant to their project-specific CO_2-rich stream and its impurities. The object of the present work is to assist designers with this step by (i) assessing critically the quality of available aqueous dew point data relevant to the conditions of CO_2 compression and transportation in pipelines, (ii) testing the ability of popular thermodynamic equations of state to predict aqueous dew points of CO_2-rich mixtures, and (iii) investigating methods of maintaining single-phase conditions within CO_2 pipelines during shut-in situations.

Literature review

The data review considers the binary system CO_2 + H_2O and ternary systems consisting of CO_2 + H_2O plus compounds likely to exist as impurities in the industrial CO_2-rich mixture. Chemical solvents likely to promote H_2O solubility are also considered.

Binary system $CO_2 + H_2O$

An extensive review of the thermodynamic literature was conducted to identify data relating to fluid-fluid equilibria of the CO_2 + H_2O binary system. In total, more than 130 references were identified containing data on the solubility of CO_2 in H_2O-rich phase and/or the solubility of H_2O in CO_2-rich phase. The majority of the data and references related to the composition of the aqueous phase and are not relevant to the present work. However, approximately 750 data points were found relating to the H_2O content of the CO_2-rich phase at equilibrium. The locations of these data in the (p,T) plane are shown in Figure 1.

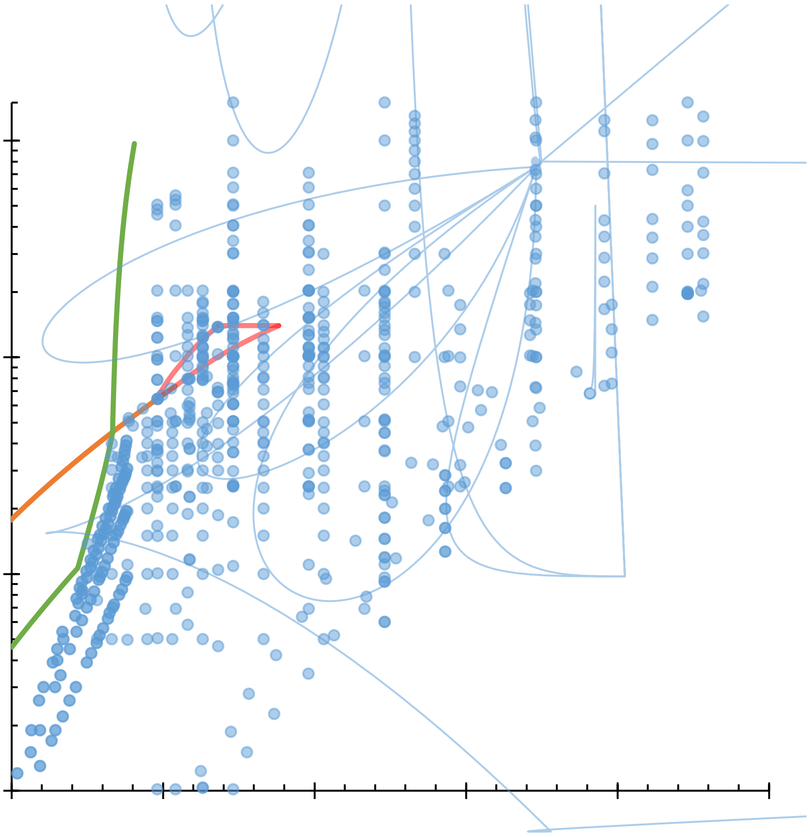

Figure 1. Pressure and temperature conditions of literature data for the solubility of H_2O in the CO_2-rich phase for the binary CO_2 + H_2O system. The saturation pressure curve of pure CO_2 is shown together with the hydrate boundary calculated using the software package Multiflash (Infochem, 2014). The approximate (p,T) region corresponding to shut-in conditions is also shown.

Once compressed to approximately 15 MPa, CO_2-rich fluids are likely to enter the pipeline network at temperatures near 330 K, although higher or lower temperatures may be encountered depending on operating and environmental conditions. In the case of prolonged shut-in, the pipeline will cool to ambient conditions that will vary geographically and seasonally. From Figure 1, the risk of hydrate formation increases substantially below approximately 280 K, so this temperature is taken as the lower limit of possible pipeline cooling during shut-in. Therefore, a total of 36 literature references (Table 1) were classified as containing data on the solubility of H_2O in CO_2-rich fluids relevant to pipeline conditions.

Table 1. Recommended and rejected data for the aqueous dew point of the CO_2-rich phase in the CO_2 + H_2O binary system ($280 < T$ /K < 348, $p < 15$ MPa).

Recommended data	**Rejected data**
Wiebe and Gaddy, 1941	Tödheide and Franck, 1963
Sidorov et al., 1953	Gillespie and Wilson, 1982
Coan and King, 1971	Sayegh and Najman, 1984
Verbrugge, 1979	Patel et al., 1987
Chrastil, 1982	Sako et al., 1991
Smith et al., 1985	Feng and Hou, 1993
Nakayama et al., 1987	Cai and Wu, 1996
Song and Kobayashi, 1987	Valtz et al., 2004
Briones et al., 1987	Hou et al., 2013 (dense phase)
Ohgaki et al., 1988	Jiang et al., 2014
D'Souza et al., 1988	Comak et al., 2016
King et al., 1992	
Dohrn et al., 1993	
Jackson et al., 1995	
Bamberger et al., 2000	
Jarne et al., 2004	
Iwai et al., 2004	
Koglbauer and Wendland, 2008	
Seo et al., 2011	
Kim et al., 2012	
Wang et al., 2013	
Hou et al., 2013 (vapour-phase)	
Song et al., 2014	
Foltran et al., 2015	
Meyer and Harvey, 2015	
Loring et al., 2017	

Ternary systems $CO_2 + H_2O + X$

The likely impurities in CO_2-rich streams generated from natural gas sources are predominantly hydrocarbons from the produced reservoir fluid. This contamination is typically on the order of (0.5 to 4) mole% and may include BTEX compounds up to 1000 ppm depending on the current performance of the acid gas removal unit (AGRU). Nitrogen (N_2) may also be present in the feed stream and/or remain in the system after commissioning, which may affect the water dewpoint of the CO_2 rich stream.

The literature review located about 20 references with phase equilibrium data for ternary mixtures containing CO_2 + H_2O with N_2, alkanes or aromatic compounds (Table 2). The number of relevant data for the aqueous dew points of CO_2-rich phases is quite small. Many of the available ternary data relate to the composition of the aqueous phase or to a phase rich in hydrocarbon. Of the data related to the CO_2-rich phase, many are at lower (e.g. Jarne et al., 2004) or higher temperatures (e.g. Brandt et al., 2000; Forte et al., 2011; Al Ghafri et al., 2014; Al Ghafri et al., 2015) than are relevant to CO_2 pipeline conditions.

Table 2. Number of references and phase equilibrium data for ternary mixtures of CO_2 + H_2O + X, where X is N_2 or a hydrocarbon compound.

Substance (X)	**Reference**	**# CO_2-rich phase**	**# Aqueous phase**	**# Hydrocarbon-rich phase**
N_2	Zel'venskii, 1939	0	48	0
	Liu et al., 2012	42[a]	42	0
	Foltran et al., 2015	14	0	0
CH_4	Sharma, 1969	0	0	30
	Song and Kobayashi, 1990	6	0	0
	Dhima, 1998	0	9	0
	Servio et al., 1999	0	17	0
	Jarne et al., 2004	51	0	81
	Qin et al., 2008	0	21	0
	Al Ghafri et al., 2014	38	54	16
	Fouad et al., 2015	13	0	29
	Chapoy et al., 2016	0	0	12
	Loring et al., 2017	1	0	3
C_2H_6	Jarne et al., 2004	31	0	25
	Fouad et al., 2015	21	0	0
C_3H_8	Gil et al., 2006	20	0	0
	Forte et al., 2013	0	16	16
n-heptane	Al Ghafri et al., 2015	26	26	26
n-decane	Forte et al., 2011	40	40	40
	Rocha et al., 2013[b]	0	0	0
Benzene	Brandt et al., 2000	129	68	0
Toluene	Pfohl et al., 1997	5	12	7
	Pfohl, 1998	2	2	0

[a] Composition given on ‘water-free’ basis
[b] Sampling of phases not performed

Polar solvents may be beneficial for maintaining single phase conditions in pipelines by enhancing the solubility of H_2O in the CO_2-rich stream. A literature survey was conducted for ternary mixtures containing solvents including methanol, ethanol (EtOH), isopropyl alcohol and acetone. Only the CO_2 + H_2O + EtOH ternary system was identified as having sufficient numbers of available data near the conditions of interest to CO_2 pipelines. A summary of the data situation for the ternary system CO_2 + H_2O + EtOH is given in Table 3.

Table 3. Number of phase equilibrium data for the CO_2 + H_2O + Ethanol ternary system in the literature.

Reference	**# CO_2-rich phase**	**# other phase**
Kreim, 1983	20	20
Gilbert and Paulaitas, 1986	29	29
Takishima et al., 1986	7	13
Feng et al., 1988	17	17
Nagahama et al., 1988	7	22
Furuta et al., 1989	18	18
Inomata et al., 1989	41	41
de la Ossa et al., 1990	27	27[a]
Cho et al., 1991	74	74
Di Giacomo, 1991	27	0
Cho et al., 1993	27	27
Feng and Hou, 1993	5	5
Hirohama et al., 1993	15	15
Horizoe et al., 1993	20	10
Lim et al., 1994	108	108
Yao et al., 1994	15	15
Yoon et al., 1994	6	6
Lim et al., 1995	15	15
Zhou and Wang, 1996	0	29
Kim et al., 1997	12	12
Chen et al., 2000	9	9
Budich and Brunner, 2003	15	15
Yao et al., 2004	17	0
Dalmolin et al., 2006	0	124
de la Fuenta et al., 2007	0	11
Durling et al., 2007	38	38
Fornari et al., 2009	4	4
Bejerano et al., 2015	7	7
Maeta et al., 2015	4	4

[a] CO_2-free basis

Data assessment

The relatively large number of fluid phase equilibrium data available for the CO_2 + H_2O binary system permits thorough assessment of their relative quality. These were analyzed using the stringent consistency test developed by Heck and Hiza (1967), known as the method of enhancement factors. The data relating to the diffuse and dense CO_2-rich phases were assessed by calculating the enhancement factor, *f*, defined in terms of the mole fraction of water in the CO_2-rich phase, $y_{\mathrm{H_2O}}$, the mixture pressure, *p*, and the saturation pressure of pure water at the specified temperature $p_{\mathrm{H_2O}}^{sat}$:

$$f = \frac{y_{\mathrm{H_2O}} p}{p_{\mathrm{H_2O}}^{sat}}$$

The nature of this definition means that as $p \rightarrow 0$, $f \rightarrow 1$; data which do not exhibit this limiting behaviour can be excluded as being of low quality. The quality of the available data was assessed by plotting f for several isotherms in the temperature range of interest (280 to 348) K. Examples of the enhancement factor analysis are shown in Figures 2 and 3 for isotherms near (298 and 323) K (figures for other temperatures are shown in the Supplementary Material).

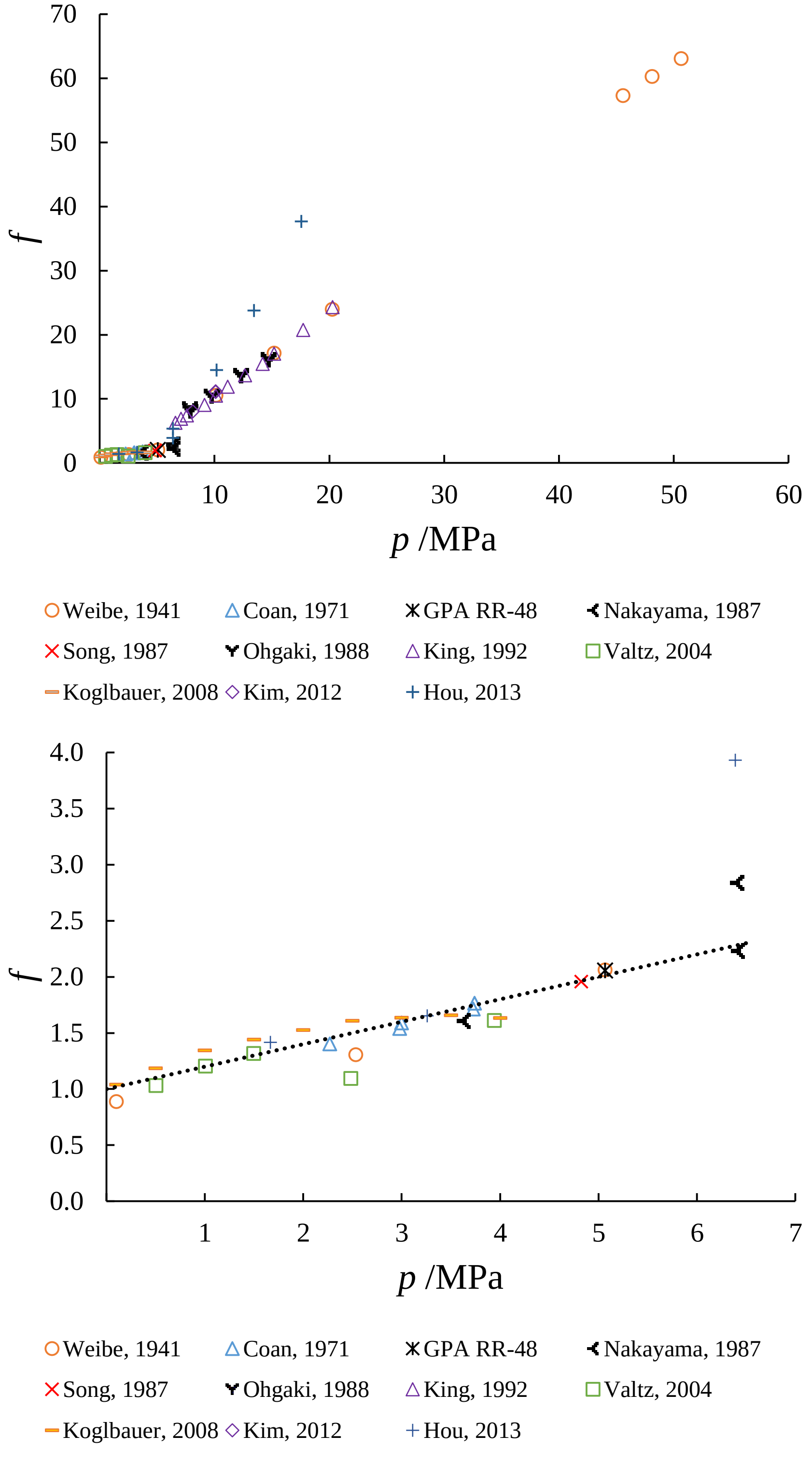

Figure 2. Enhancement factor analysis for data measured near 298 K for the $CO_2 + H_2O$ binary. Dotted line is a guide consistent with $f(P = 0) = 1$.

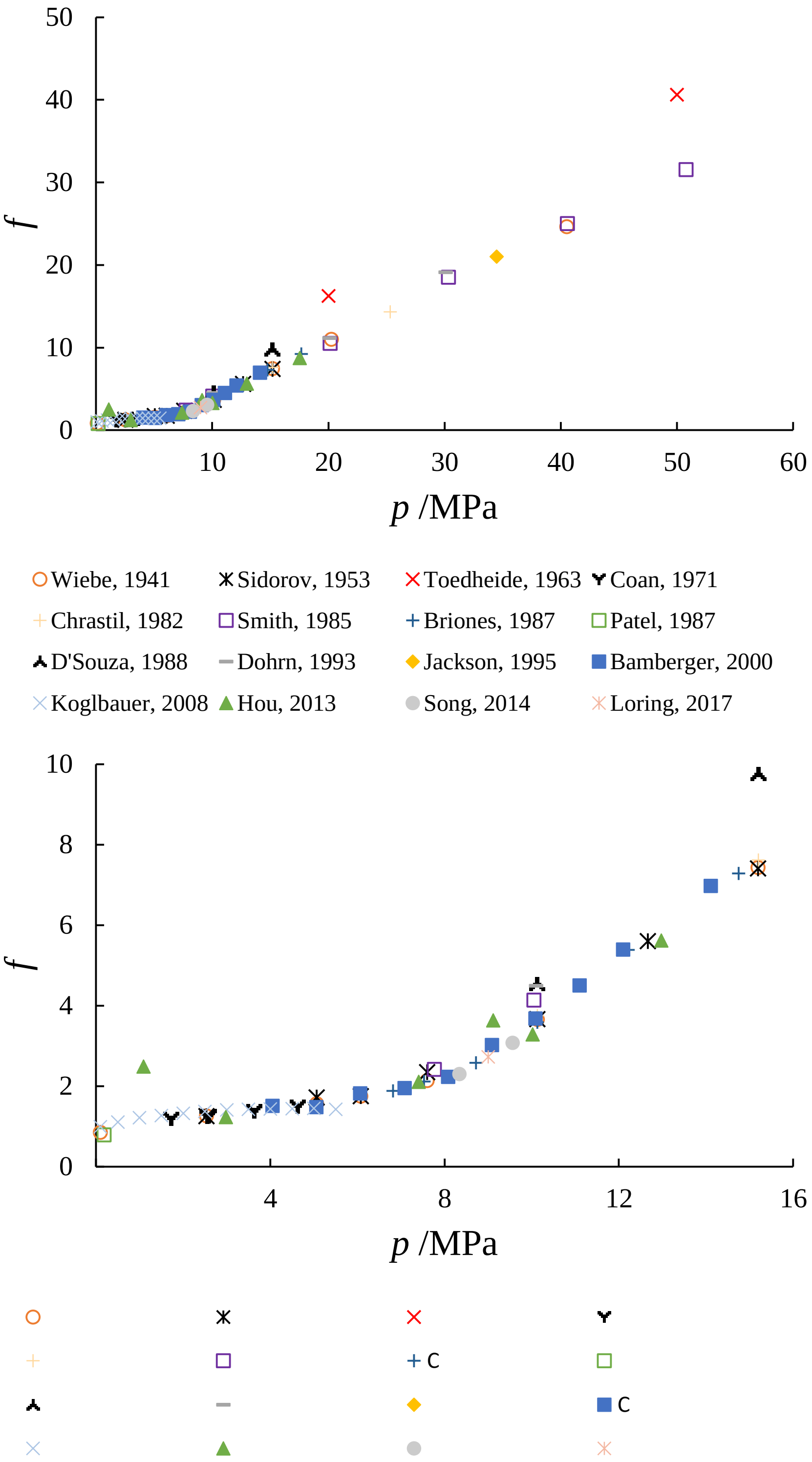

Figure 3. Enhancement factor analysis for data measured near 323 K for the $CO_2 + H_2O$ binary.

Based on the analysis of enhancement factors, the available data for H_2O solubility in CO_2-rich sub- and super-critical phases were categorised as either ‘Recommended’ (those having few or minor inconsistencies) or ‘Rejected’ (those having many or large inconsistencies). Of 37 data sets from 36 references, 26 data sets were recommended as being of good quality and 11 were rejected as being of poor quality (Table 1). The relatively small number of relevant available data for each ternary mixture prohibits meaningful consistency tests.

Results of comparisons with thermodynamic models

A range of thermodynamic models were chosen for comparison with the available experimental aqueous dew point data in the binary system CO_2 + H_2O. The following six models were selected either because they were thought likely to perform reasonably well in the description of these properties and/or because they are widely used by industry and compatible with dynamic simulations of the process:

- Multiflash RKS (Advanced) ('Advanced' Redlich-Kwong-Soave EOS) (Infochem, 2014)
- Multiflash CPA-Infochem (Cubic Plus Association EOS) (Infochem, 2014)
- AspenTech HYSYS Peng Robinson EOS (AspenTech, 2016)
- TREND 3.0 EOS-CG (combustion gas multi-parameter EOS) (Span et al., 2016; Gernert and Span, 2016)
- NIST REFPROP 9.1 (GERG EOS) (NIST, 2013)
- PSE gPROMs SAFT-γ-Mie (Statistical Associating Fluid Theory with Mie potential) EOS (PSE, 2015)

Figures 4 and 5 show predictions of H_2O solubility in CO_2-rich phases from three of the selected thermodynamic models near (298 and 323) K, respectively. Recommended data at these conditions are also shown.

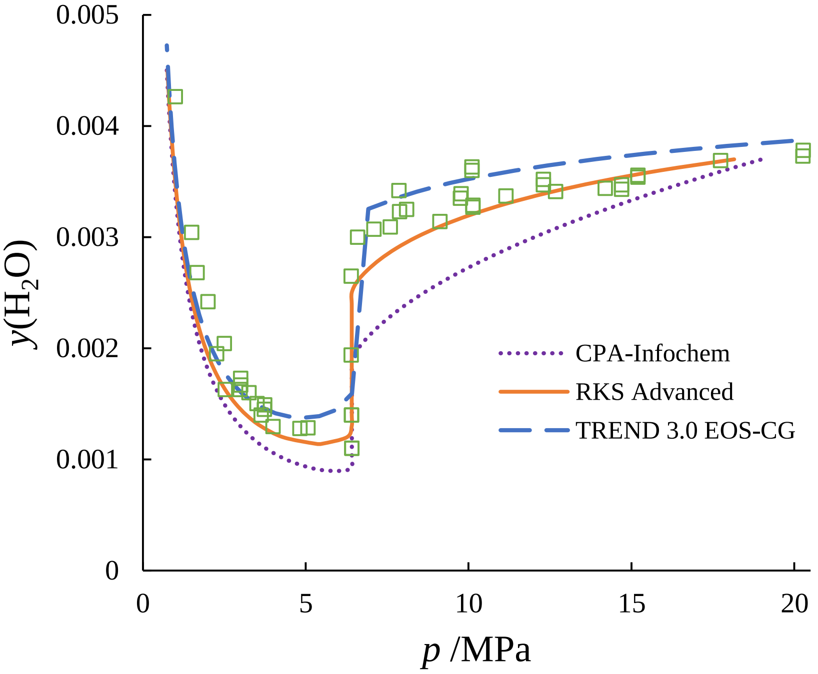

Figure 4. Aqueous dew point predictions from thermodynamic models and recommended data for the binary system CO_2 + H_2O near 298 K (Table 1).

Figure 5. Aqueous dew point predictions from thermodynamic models and recommended data for the binary system CO_2 + H_2O near 323 K (Table 1).

The CPA(Infochem) model under-predicts systematically the solubility of H_2O in the CO_2-rich phase, with deviations reaching approximately 30 % near 323 K and 15 MPa. The predictions with the RKS (Advanced) implemented in the same software package also tend to be conservative; however the magnitude of the deviations is considerably smaller than CPA(Infochem). The EOS-CG results are the least conservative with the model marginally over-predicting the solubility of H_2O in the CO_2-rich phase.

The other thermodynamic models that were tested gave less satisfactory results. The SAFT-γ-Mie model over-predicted the H_2O solubility of the dense CO_2 by (10 to 20) %. Deviations with the HYSYS Peng-Robinson model were even larger: predicted H_2O solubilities are up to an order of magnitude too large. The multiparameter Helmholtz EOS based on the GERG-2008 equation of state implemented in REFPROP exhibited unacceptable convergence behaviour, especially in the dense fluid-fluid region (i.e. at pressures above the critical pressure of pure CO_2).

Overall, the RKS (Advanced) model gives the best results. Its predicted aqueous dew points are conservative but not overly so, which is beneficial for process design, and agreement with data is highly satisfactory over the full temperature range of interest. For this reason, only RKS (Advanced) –

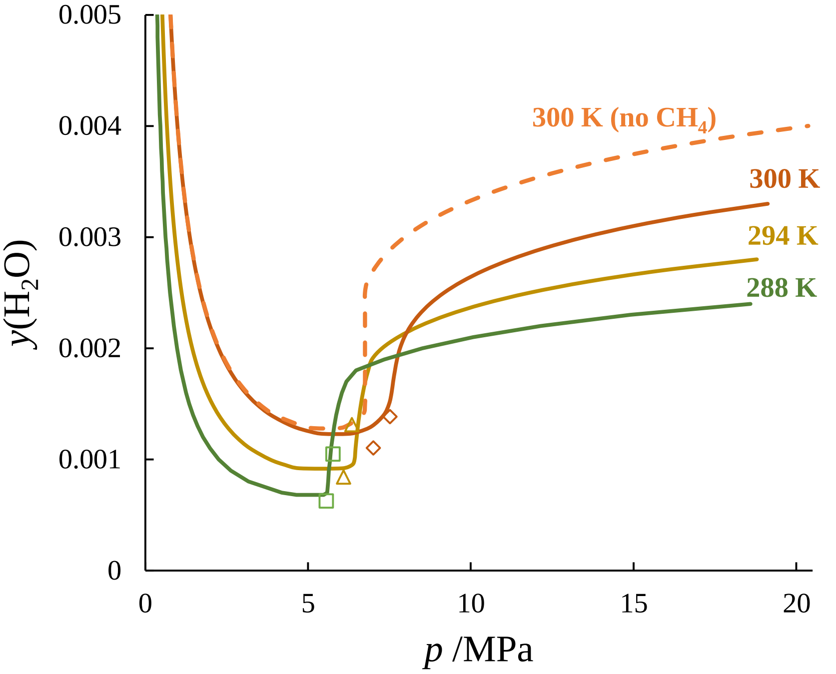

Figure 6. Equilibrium H_2O content of the ternary system $CO_2 + H_2O + CH_4$, where the methane mole fraction was 0.0531 at 300 K, 294 K and 288 K. The data were measured by Song & Kobayashi (1987) and the solid curves were calculated with the RKS (Advanced) EOS in Multiflash. The dashed curve corresponds to the calculated aqueous dew point of the CO_2 + H_2O binary mixture at 300 K.

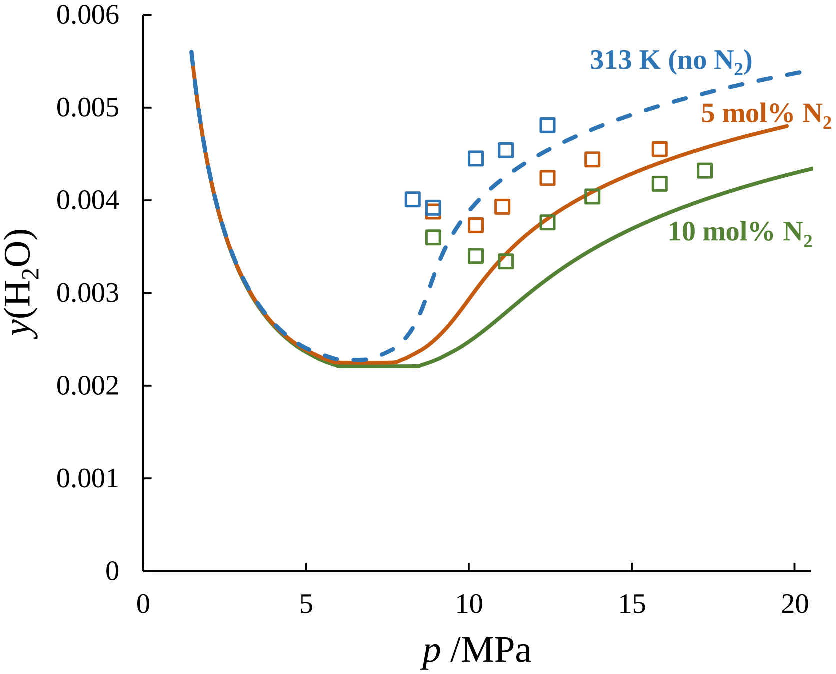

Figure 7. Equilibrium H_2O content of the ternary system $CO_2 + H_2O + N_2$ at 313 K where the N_2 mole fraction was 0 (blue symbols & dashed curve), 0.05 (orange symbols and curve) and 0.10 (green symbols and curve). The data were measured by Foltran et al. (2015) and the curves were calculated with the RKS (Advanced) EOS in Multiflash.

The overall effects of CH_4 and N_2 on the solubility of H_2O in CO_2-rich fluids are similar. In the low-pressure region, compared to the situation of pure CO_2, the presence of 0.05 mole fraction of impurity is not predicted to have significant effect on the solubility of H_2O. However, in the high-pressure region where density of the CO_2-rich fluid is larger, the presence of impurities causes the solubility of H_2O to decrease considerably. Compared to pure CO_2, fractions of CH_4 or N_2 near 0.05 are predicted to decrease the solubility of H_2O by (10 to 20) %. These predictions are in good qualitative agreement with the experimental values of Song and Kobayashi (1987) and Foltran et al. (2015).

Effect of polar solvents

Literature data for ternary systems of CO_2 + H_2O + polar solvent are also scarce. Sufficient literature data for CO_2-rich fluids were only identified for the CO_2 + H_2O + EtOH ternary system. The impact of the addition of EtOH on the H_2O dew point of the CO_2-rich fluid has been investigated by examining a selection of the available phase equilibrium data (Figure 8).

Figure 8(a) shows that the representation of the experimental data for this ternary by the Multiflash RKS (Advanced) EOS is poor, as may be expected for a system containing two strongly polar compounds. The two-phase region predicted by the Multiflash RKS (Advanced) EOS is much larger than the experimental one. The experimental data in Figure 8(a) show that if the mole fraction of EtOH is above 0.4, any mole ratio of CO_2 and H_2O will result in a single phase fluid, whereas according to predictions made with the EOS, the fraction of EtOH necessary to ensure single phase conditions is close to 0.6. Furthermore, the CO_2 + EtOH binary is erroneously predicted by the RKS (Advanced) EOS to be two-phase at some mole fractions. Durling et al. (2007) suggest that the Peng Robinson EOS coupled with the Wong-Sandler mixing rules could be used to correlate the experimental data well.

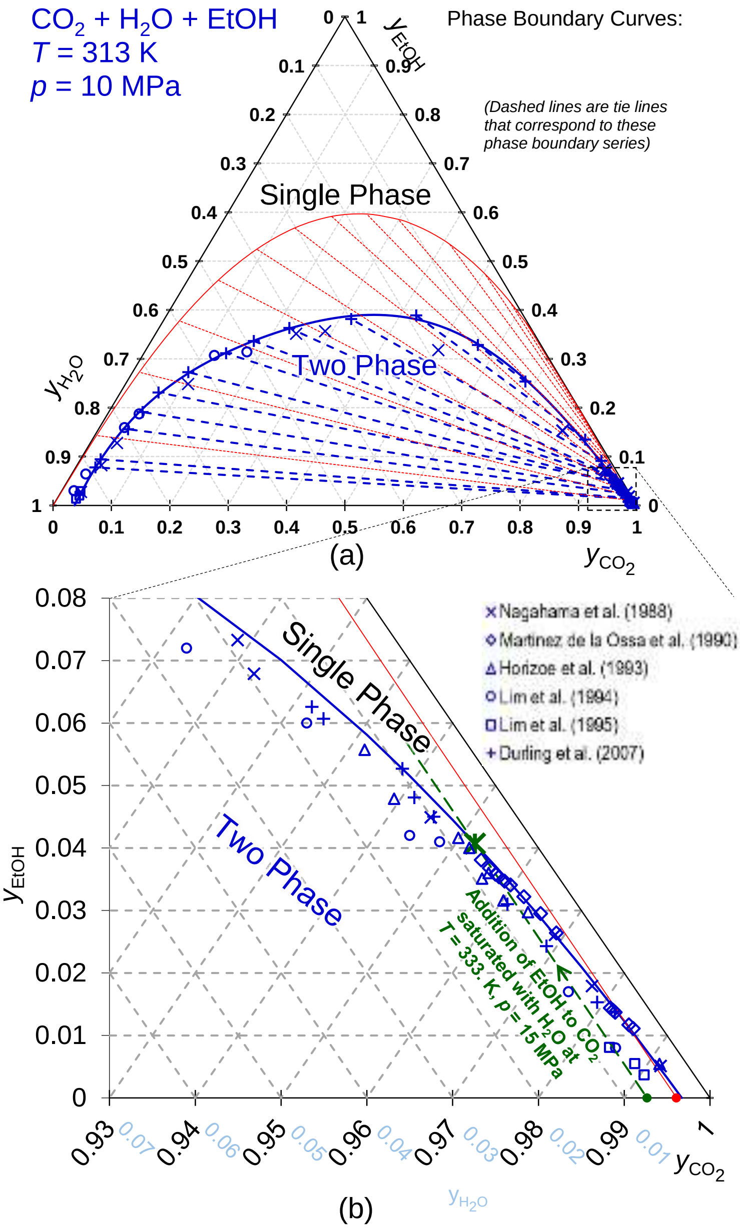

Figure 8. (a) Ternary triangular phase equilibrium diagram for CO_2 + H_2O + EtOH at T = 313 K and p = 10 MPa. The thick blue curve is the measured phase boundary of Durling et al. and the thin red curve is the phase boundary calculated using the Multiflash RKS (Advanced) EOS. The dashed lines represent tie lines. (b) Inset of CO_2-rich region: Literature data are points (except the red and green filled points which are binary CO_2 + H_2O mixture dew points calculated using the Multiflash RKS (Advanced) EOS at (313 and 333) K, respectively). The green dashed line represents the addition of EtOH to a mixture of 0.99265 CO_2 + 0.00735 H_2O (the H_2O saturation mole fraction at T = 333 K and p =15 MPa). This dashed line intersects the phase boundary (solid blue curve) at an EtOH mole fraction of about 0.041, suggesting that the addition of this much EtOH would keep the mixture single phase, even as it cooled from (333 to 313) K. The experimental data of Lim et al (1994), Lim et al (1995) and Durling et al. (2007) suggest that the required mole fraction of EtOH needed to keep the H_2O in the CO_2-rich phase could be significantly less than 0.041.

Case Study: Dew Point Control in CO_2 Pipelines

The experimental data in Figure 8(a) confirm that a sufficient dose of EtOH to a CO_2-rich stream can enhance H_2O solubility and maintain single phase conditions. The minimum amount of EtOH likely to be required to be dosed into an industrial pipeline for such an application is investigated in the following case study.

Consider a pipeline containing a (water-saturated) binary mixture of 0.99265 CO_2 + 0.00735 H_2O at T = 333 K and p = 15 MPa. Under shut-in conditions, the confined fluid will cool isochorically. Upon cooling to T = 313 K and p = 10 MPa (an approximately isochoric path), the mixture is expected to split into two phases, as indicated by the location of the green point in Figure 8(b). The green dashed line in Figure 8(b) signifies injection of EtOH into the CO_2 + H_2O mixture. The point of intersection between the green line and the blue saturation curve represents the amount of EtOH required to prevent phase separation. In the case of a mixture with a H_2O to CO_2 molar ratio of 0.0074, the lines intersect at a required EtOH mole fraction of 0.041. This calculation is based on the intersection of the green and blue curves, where the blue saturation curve represents a 'worst-case' situation. If one were instead to use the experimental data of Lim et al (1994), Lim et al (1995) and Durling et al. (2007), which suggest that the water dew point is to the left of the solid blue curve in Figure 8(b), the amount of EtOH required to keep the system single phase could be significantly less.

Assuming a pipeline volume of 1000 m^3, estimates of quantities of ethanol required to maintain single-phase states for CO_2-rich fluids under different conditions have been calculated and are shown in Table 4. The first situation (row) is based on the worst-case behaviour shown in Figure 8(b), in which the system cools from an initial condition of T = 333 K and p = 15 MPa to T = 313 K and p =10 MPa. The volume of EtOH required to be injected into the pipeline network is approximately 35 m^3, or 3.5 % of the volume of the network. In the next two rows of Table 4, the same ratio of EtOH to H_2O is assumed to keep the fluid single phase. In the second row, the initial condition is T = 313 K and p =15 MPa, so the required amount of EtOH increases because the amount of CO_2 is larger. In the third row, the amount of water present has been reduced to a level around 2000 mg / std m^3 for an initial condition of T = 313 K and p = 15 MPa. Under the assumption that the ratio of EtOH to H_2O required to stay in a single phase condition remains at 5.8, approximately 11.6 tonnes of EtOH would need to be injected (only 1.5 % of the volume of the network).

Table 4. Estimated mass and volume of ethanol required to keep pipeline single-phase.

T_{init} K	p_{init} MPa	V_{pipe} m^3	CO2 $kg \cdot m^{-3}$	m_{CO2} tonne	y_{H2O}	y_{EtOH}	m_{EtOH} tonne	V_{EtOH} m^3
333	15	1000	604.1	604	0.007	0.041	27.2	34.6
313	15	1000	780.2	780	0.007	0.041	35.1	44.7
313	15	1000	780.2	780	0.0025	0.014	11.6	14.8

Discussion

The RKS (Advanced) EOS predicts the solubility of H_2O in CO_2-rich phases very well. Inspection of the binary interaction parameters between the components CO_2 and H_2O in Multiflash reveals the likely reason for this success: the binary interaction parameters are represented by a temperature-dependent function having three tuned coefficients, viz

$$k_{ij} = 1 - (0.1387397 + 0.000241538T - 1.95236\times10^{-7}T^{2})$$

This gives the RKS (Advanced) EOS significantly greater flexibility than the Peng-Robinson equation implemented in HYSYS, which has a temperature-independent binary interaction parameter between CO_2 and H_2O.

In addition to their well-known high computational cost, which already places them at disadvantage compared to cubic EOS, it seems apparent from this investigation that multiparameter Helmholtz EOS such as GERG-2008 and EOS-CG are not as well-suited for use in process simulations due to convergence issues. This is despite the fact that these multiparameter models ought to be able to represent the properties of mixtures such as CO_2 + H_2O more accurately than simple cubic EOS. Multi-parameter Helmholtz EOS are in general more accurate at representing the single-phase properties of mixtures for which they were developed. While this is beyond the scope of this review, Efika et al. (2016) found that the density predictions of the EOS-CG for saturated CO_2 + H_2O binaries were slightly better than the predictions of the cubic EOS by Spycher and Pruess (2010) over the temperature range (293 to 450) K and at pressures to 64 MPa.

Although not unexpected, one of the main disadvantages of the RKS (Advanced) equation of state identified in this work was the inability to represent accurately the enhancing effect that EtOH has on the solubility of H_2O in the CO_2-rich phase. It is likely that this deficiency could be redressed by tuning temperature-dependent binary interaction parameters for the binary subsystems CO_2 + EtOH and H_2O + EtOH based on data in the literature. This was beyond the scope of the present work but represents an opportunity for future improvement.

Conclusions

The literature on the aqueous dew points in the CO_2 + H_2O binary system and related ternary systems has been reviewed. Twenty-six data sets were found to be of good quality and are recommended for the purposes of EOS development and process design at conditions relevant to CO_2 pipelines. The RKS (Advanced) EOS from Multiflash was best able to predict the solubility of H_2O in CO_2-rich phases. Multiparameter Helmholtz EOS were problematic and many issues related to convergence were encountered, especially for mixtures at high pressure where dense fluid-fluid equilibria occur.

Acknowledgements

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