

# **SECTION 1**

## **DATA AND CORRELATION**

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# Prediction of Acid Gas Dew Points in the Presence of Water and Volatile Organic Compounds

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## ***Abstract***

Aromatic hydrocarbons which are present in sour natural gas streams can be absorbed into the amine treating solution at the bottom of the contactor and exit in the rich amine stream. Depending on the process configuration, these dissolved hydrocarbons can end up in the acid gas leaving the amine regenerator. In acid gas injection facilities, trace amounts of heavy hydrocarbons in the acid gas may lead to the formation of a sour hydrocarbon liquid phase in the compressor interstage scrubbers.

In this exploratory work, a cubic equation-of-state (EOS) model was used to make predictions of non-aqueous ( $L_1$ ) dew points in acid gas systems. The objective was to develop a better understanding of the conditions under which this phenomenon can occur, and to reinforce the need for accurate experimental vapor-liquid equilibrium data to support cost effective design and model development.

## **1.1 Introduction**

Benzene, toluene, ethyl benzene and xylene isomers are commonly referred to collectively as BTEX compounds. These compounds are known to be toxic to humans and their containment and disposal are of special interest to the hydrocarbon industry. BTEX environmental contamination is often linked to leakage from underground gasoline storage tanks or accidental spills. Awareness of this toxicity led to regulated clean air emission standards that directly impact

## 4 CO<sub>2</sub> SEQUESTRATION AND RELATED TECHNOLOGIES

the natural gas processing industry as trace amounts of BTEX compounds are associated with produced fluids such as natural gas.

Sour gas production generally involves a subsequent processing step in which the hydrogen sulphide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) are removed to produce an acid gas stream that may be a candidate for acid gas injection. Liquid solvents that are used to remove the H<sub>2</sub>S and CO<sub>2</sub> from the gas stream are often aqueous solutions of organic chemicals that have a high affinity for the BTEX compounds.

Distribution of the BTEX compounds within the various streams of a natural gas processing plant is a complex phenomenon involving many interrelated process variables such as operating pressures and temperatures, amine composition, amine circulation rates, and others. Of particular interest in acid gas injection, is the amount of BTEX compounds that end up in the acid gas product leaving the amine regenerator.

The presence of trace quantities of BTEX compounds in the acid gas, if unaccounted for at the design stage, may lead to the unexpected formation of a sour non-aqueous liquid phase in the compressor train, and considerable operational difficulties. The objective of this work was to develop a better understanding of the conditions under which this phenomenon can occur, and to reinforce the need for accurate experimental vapor-liquid equilibrium data to support cost effective design and model development.

### 1.2 Previous Studies

In order to estimate the levels of BTEX compounds that will be present in the acid gas, there is a need for accurate vapor-liquid equilibria (VLE) and/or vapor-liquid-liquid equilibria (VLLE) data for BTEX and similar hydrocarbons in amine treating solutions under rich amine conditions. Operating plant data are also useful to verify the predictions of any thermodynamic model.

Ng et al. (1999) provided an overview of specific phase equilibria data and physical properties that are required for reliable design of acid gas injection facilities. Hegarty and Hawthorne (1999) presented valuable operating data for a Canadian gas plant using MDEA in which measured BTEX compositions were reported. McIntyre et al. (2001) and Bullin and Brown (2004) tabulated the experimental data available for hydrocarbon and BTEX solubility in amine treating solutions and demonstrated general trends

in amine plant BTEX absorption using computer simulation. Valtz et al. (2002) presented a comprehensive set of fundamental solubility data for aromatic hydrocarbons in aqueous amine solutions. Miller and Hawthorne (2000) and Jou and Mather (2003) measured the solubility of BTEX compounds in water.

Clark et al. (2002) measured bubble and dew points for a nominal 10 mol%  $H_2S$ /90 mol%  $CO_2$  mixture and regressed an equation of state to match the phase envelope. Satyro and van der Lee (2009) demonstrated that with suitable modification to interaction parameters, a cubic equation of state can provide reliable predictions of phase behavior in sour gas mixtures.

### 1.3 Thermodynamic Model

A rigorous treatment of the complex phase behavior in the  $H_2S$ - $CO_2$ -water-BTEX system was beyond the scope of this work, which was intended to be exploratory in nature. The Peng-Robinson equation-of-state with classical van der Waals mixing rules was used in this study. The interaction parameter for the  $H_2S$ - $CO_2$  binary was set to 0.1 and all others were set to zero. Table 1 contains the critical properties used for the system components.

**Table 1.** Component critical properties.

Component	Critical P, kPa	Critical T, °C	Acentric Factor	Molecular Weight
Hydrogen Sulphide	9007.8	100.45	0.1	34.076
Carbon Dioxide	7386.6	31.05	0.225	44.01
Benzene	4898.0	289.0	0.2092	78.112
Toluene	4105.8	318.7	0.2637	92.138
Ethyl Benzene	3605.9	344.1	0.3026	106.165
o-Xylene	3734.2	357.2	0.3118	106.165
m-Xylene	3536.3	343.9	0.3255	106.165
p-Xylene	3510.8	343.1	0.3211	106.165

The performance of the Peng-Robinson equation of state has been well documented in the literature. The model reproduced the dew point locus of Clark et al. (2002) to within 2.5%.

## 1.4 Calculation Results

The conditions of the calculations were chosen to encompass those normally found in acid gas injection compression: pressures from 150 kPa to 10 MPa, and temperatures above the hydrate formation curve from 0° to 100°C. Three different nominal acid gas compositions were considered: 20/80, 50/50, and 80 mole% H<sub>2</sub>S/20 mole% CO<sub>2</sub>. Hydrocarbon components studied included: benzene, toluene, ethyl benzene and dimethyl benzenes (xylenes).

The model was used to generate the phase envelope for each of the three nominal acid gas compositions. The influence of associated water on the location of the bubble and dew-point loci was not considered in this work. A typical injection profile was generated for each nominal composition using a starting pressure of 150 kPa and constant compression ratio. Temperatures in the compression process were restricted to remain under 150°C. Cooling temperature was set to 50°C. The final pressure was selected to be under 10 MPa but above the mixture critical point.

Initial calculations indicated that the phase behavior of the acid gas mixtures in the presence of each of the three xylene isomers was similar. For simplicity only o-xylene was considered in this study.

To establish a reasonable range of BTEX compositions, a sensitivity study was undertaken using pure H<sub>2</sub>S. The model was used to determine the L<sub>1</sub> dew point temperature at 4000 kPa using various compositions of benzene and o-xylene ranging from 0 to 5000 ppmv. The results are shown in Figure 1.<sup>1</sup> Below concentrations of 100 ppmv, the aromatic compounds increase the dew point temperature by less than 1°C. Hegarty and Hawthorne (1999) reported BTEX content of up to 2500 ppmv in the acid gas of an operating MDEA plant. Using this as a guideline, non-aqueous liquid (L<sub>1</sub>) dew points were calculated for each of the three nominal acid gas compositions with 500-, 2000- and 5000 ppmv of each of the four aromatic compounds.

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<sup>1</sup> Figures 1 through 4 appear at the end of this paper.

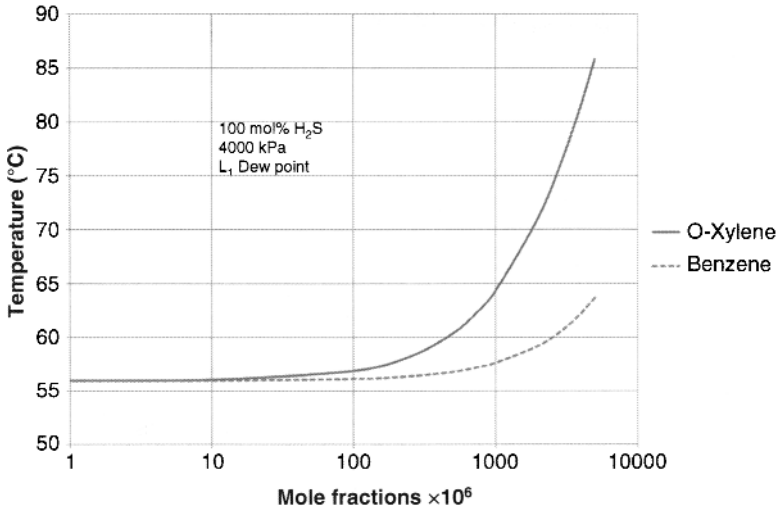


Figure 1. Effect of BTEX compounds on  $L_1$  dew point in pure  $H_2S$ .

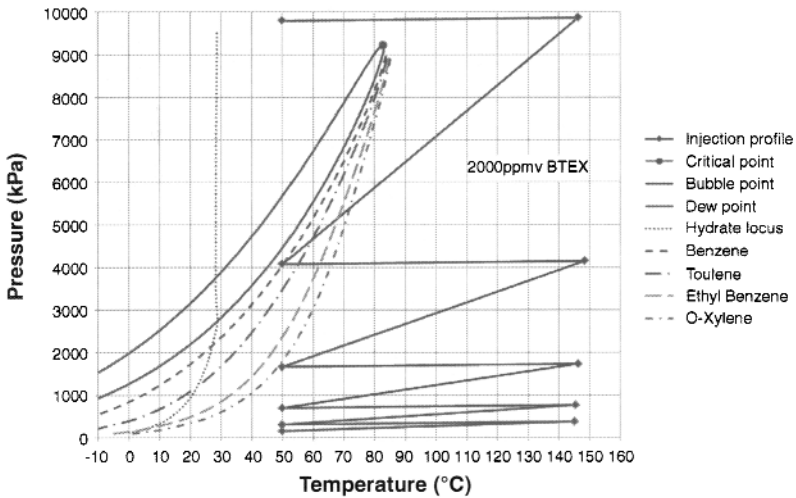
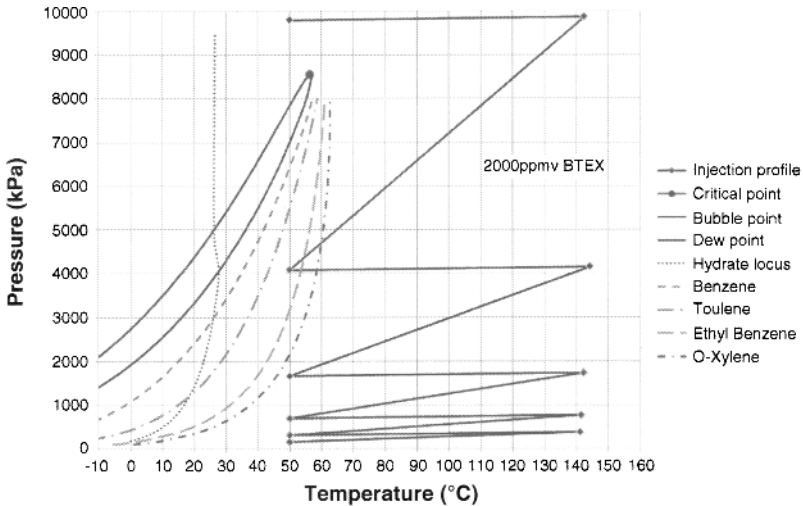


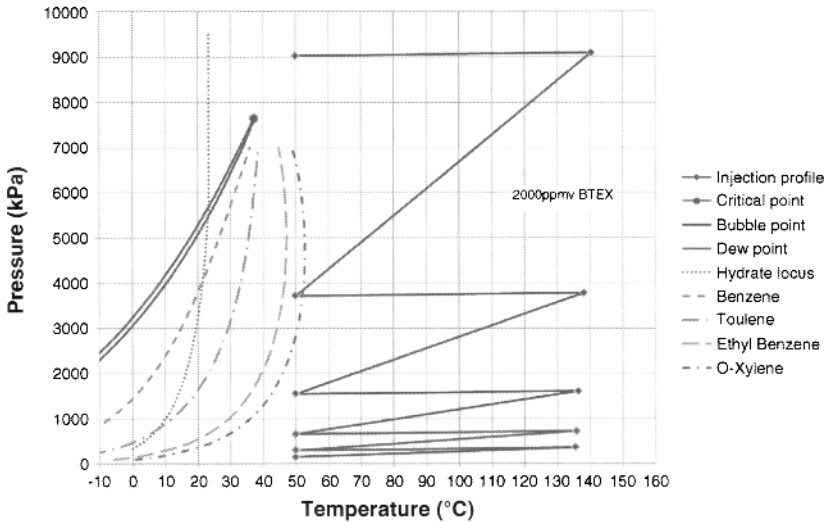
Figure 2. Effect of BTEX compounds in 80%  $H_2S$  - 20%  $CO_2$ .

Clearly this range of calculated points generated a significant amount of data. The results for the 2000 ppmv cases are presented in Figures 2 through 4 and provide an adequate representation of the general trends that were observed. Note that curves labeled as organic compounds represent the dew point loci for the acid gas mixture with 2000 ppmv of only that organic compound.

## 8 CO<sub>2</sub> SEQUESTRATION AND RELATED TECHNOLOGIES



**Figure 3.** Effect of BTEX compounds in 50% H<sub>2</sub>S - 50% CO<sub>2</sub>.



**Figure 4.** Effect of BTEX compounds in 20% H<sub>2</sub>S - 80% CO<sub>2</sub>.

Using data from McIntyre et al. (2001) for BTEX component distribution in the acid gas from an MDEA plant as a guideline, flash calculations were performed at 50°C for the mixture given in Table 2. Identical calculations were performed for a mixture containing 80 mol% H<sub>2</sub>S and 20 mol% CO<sub>2</sub>. The results are shown in Table 3.



**Table 2.** Composition of mixture used for condensation study.

Component	Composition, mol %
Hydrogen Sulphide	79.82
Carbon Dioxide	19.955
Benzene	1000 ppmv
Toluene	750 ppmv
Ethyl Benzene	250 ppmv
o-Xylene	250 ppmv

**Table 3.** Condensation study results at 50°C.

Pressure, kPa	Volume% L <sub>1</sub> , BTEX Mixture	Volume % L <sub>1</sub> , 80/20 H <sub>2</sub> S/CO <sub>2</sub>
3268.3	Dew point P	
3400	0.009	0
3600	0.031	0
3800	0.074	0
4000	0.169	0
4200	0.420	0
4400	1.29	0
4466.6		Dew point P
4600	3.90	2.46
4800	8.55	7.29
5000	15.6	14.2
5200	26.6	24.8
5400	45.4	42.5
5600	82.8	77.2
5654.1	Bubble point P	
5674.5		Bubble point P

## 1.5 Discussion

In the absence of experimental data for dew point conditions in acid gases with contaminants, there can be no absolute conclusions drawn on the accuracy of the predictions. This exploratory study clearly emphasizes the importance of experimental research to provide fundamental information for process design and advanced model development. The results in Figures 2 through 4 illustrate that with conservative cooling temperatures and with BTEX contaminant levels in the range of those already measured in an operating MDEA plant, it is possible to enter the three-phase region in the higher pressure interstage coolers and separators in acid gas injection facilities. More aggressive cooling escalates the potential for three-phase conditions.

The formation of a second liquid phase in the compression interstage cooling system, in itself is not a problem, provided that the phase behavior phenomenon is understood at design time. The  $L_1$  phase is less dense than water, contains up to 20 mol% BTEX and, if formed, will accumulate in the interstage separators. As pointed out by Hegarty and Hawthorne (1999), it is extremely important to obtain an accurate inlet gas composition, including an extended analysis of the  $C_{6+}$  fraction to determine the aromatic content. Once the BTEX content, if any, is identified it can be accounted for in any process design, modeling, or operational troubleshooting of downstream processes such as acid gas injection.

In spite of the purely predictive nature of the calculated results, the following general observations can be made by analyzing Figures 2 through 4. The same behavior is observed in the 500 ppmv and 5000 ppmv calculated results.

- At a given pressure, the presence of BTEX compounds in acid gas widens the phase envelope, with this effect being more pronounced in acid gases with higher CO<sub>2</sub> content.
- At a given pressure, the presence of BTEX compounds in acid gas increases the  $L_1$  dew point temperature, with this effect being more pronounced in acid gases with higher H<sub>2</sub>S content. This is, in part, a result of the shift of the acid gas phase envelope to higher temperatures in high H<sub>2</sub>S mixtures.

- At equal concentration in the acid gas and at equal pressure, BTEX compounds increase the  $L_1$  dew point temperature in the order: benzene, toluene, ethyl benzene and o-xylene with o-xylene having the most pronounced effect.
- In all cases, the possibility of non-aqueous  $L_1$  formation is highest in the separator before the final stage of compression.
- If compressed acid gas is cooled to lower temperatures (e.g. 30°C) in the compressor facility, this increases the possibility of  $L_1$  formation.
- If BTEX compounds are present in the acid gas at levels less than 100 ppmv, the acid gas dew point locus is relatively unaffected.

The dew point loci shown in Figures 2 through 4 indicate where the first droplet of  $L_1$  forms. Table 3 contains an example of the condensation behavior inside the phase envelope at constant temperature. Note that the condensation behavior of the BTEX mixture is similar to the BTEX-free system except for the deep depression of the dew point pressure. Lines of constant liquid volume % are widely spaced in this region of the phase envelope. This behavior is similar to the condensation behavior of rich gas systems. The location of the bubble point is relatively unaffected by the organic compounds.

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## 12 CO<sub>2</sub> SEQUESTRATION AND RELATED TECHNOLOGIES

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