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# Glycol Loss in a Gaseous System: Thermodynamic Assessment Test of Experimental Solubility Data

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**ABSTRACT:** Triethylene glycol (TEG) is generally used to adjust the water dew point in natural gas processes. Unfortunately, only very few sets of experimental data regarding solubilities of these humidity absorbents in supercritical natural gas components have been reported in the literature partly due to the difficulties in such very low concentration measurements. Therefore, a satisfactory accuracy of measurements is not obvious, and the reliability of the corresponding data must be checked prior to their application. In this study, we focus on presenting the results of a thermodynamic assessment test (consistency test) for experimental solubility data of triethylene glycol in supercritical methane and carbon dioxide. The Gibbs—Duhem equation in terms of pressure, fugacity coefficients, solubilities of triethylene glycol in gas phase, and compressibility factor of gas phase is applied for the consistency test. The Soave—Redlich—Kwong (SRK) equation of state (EoS) along with the van der Waals (vdW2) mixing rules is used to represent the corresponding solubilities. The results show that three sets of the four investigated experimental data sets are thermodynamically consistent, while one data set is not fully consistent.

## 1. INTRODUCTION

The formation of water condensates and gas hydrates, corrosion of process facilities, and excess pressure drops in pipelines are among the inevitable problems of the existence of water in natural gas processes or enhanced oil recovery projects with carbon dioxide.[1−5] To avoid the aforementioned problems, glycols (mostly triethylene glycol) are injected into the wet gas stream in dehydration units to absorb the gas humidity and adjust the water dew-point temperature.[1,2,5−16] Substantial triethylene glycol quantities may be dissolved in the gas stream.[1,5,6] These vaporization losses in gas flows may result in higher transmission/production costs of natural gas streams.[2] Furthermore, there is evidence regarding the retrograde condensation of triethylene glycol in pipelines due to changes in operational conditions.[2] Therefore, it may lead to excess pressure drops in processes.[2]

A preliminary literature review shows that, although the experimental data of solubilities of methane, ethane, and carbon dioxide in aqueous triethylene glycol have been well-reported in the literature, the corresponding data of solubilities of triethylene glycol in supercritical methane and carbon dioxide are very scarce. They are probably limited to the measurements of Yonemoto et al.[5,6] and Jerinić and co-workers.[1]

Therefore, thermodynamic models based on accurate experimental data of the solubility of triethylene glycol in supercritical gases are needed to reliably calculate/predict the phase behavior of these compounds during natural gas processes. As a consequence, measuring accurate experimental data on corresponding phase behaviors is of great interest. However, several error sources in experimental measurements including the calibration of pressure transducers, temperature probes, and detectors of gas chromatographs, possible errors during the measurements of phase equilibria especially those dealing with low concentrations, improper design of the equipment, and so forth may lead to erroneous experimental data or at least data with a high uncertainty.[17]

In this work, we apply a thermodynamic consistency test approach for the literature data of the solubility of triethylene glycol in supercritical methane and carbon dioxide, which are imperative for natural gas systems. It is expected that this study provides a better understanding of the solubility of glycols in natural gas systems.

## 2. THERMODYNAMIC CONSISTENCY TEST

The thermodynamic relationship, which is frequently used to analyze the thermodynamic consistency of experimental phase equilibrium data is the fundamental Gibbs—Duhem equation.[3,17−31] This equation, as presented in the literature, interrelates the activity/fugacity coefficients of all components in a given mixture. If this equation is not obeyed within the defined criteria, then the data are declared to be thermodynamically inconsistent. It means that this relation imposes a constraint on the activity/fugacity coefficients that is not satisfied by the experimental data.[3,17−31] This is due to various errors occurring during experimental work especially those dealing with high pressures, time-consuming phase transitions, compositional gradients, hysteresis, and so forth.[32,33]

The way in which the Gibbs—Duhem equation[3,17−31] is arranged and applied to the experimental data has given origin to several consistency test methods, most of them designed for

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low-pressure data. Among these are the slope test, the integral test, the differential test and the tangent-intercept test.[3,17−31] Good reviews of these methods are given elsewhere.[3,17−31]

Valderrama and co-workers[24−28] have already performed thermodynamic consistency tests on various phase equilibrium systems. Recently, Eslamimanesh and co-workers[3,17,18,29,30] have applied almost the same method for performing the thermodynamic data assessment test on significant systems encountered in the petroleum industry.[3,17,18,29,30]

The method, which is based on expressing the Gibbs−Duhem equation[3,17−31] in terms of fugacity coefficients,[3,17−31] employed here is considered as a modeling procedure. An accurate representation of the experimental data (i.e., the average deviations of the model results from experimental values are within the acceptable range according to the studied system and the desired purpose) is requested to correctly apply the data assessment test. The fitting of the experimental data allows the adjustment of some model parameters through minimizing a defined objective function.[3,17−31] The basic requirements of a proper data assessment test have been well-studied before.[3,17−31]

**2.1. Expressions.** The Gibbs−Duhem[3,17−31] equation for a binary mixture at constant temperature can be rewritten in terms of the fugacity coefficients as follows:[3,17−31]

$$\left[\frac{Z-1}{p}\right]dp = y_1 d(\ln \varphi_1) + y_2 d(\ln \varphi_2) \tag{1}$$

and rearranged as:

$$\frac{1}{p}\frac{dp}{dy_2} = \frac{y_2}{(Z-1)}\frac{d(\ln \varphi_2)}{dy_2} + \frac{(1-y_2)}{(Z-1)}\frac{d(\ln \varphi_1)}{dy_2} \tag{2}$$

or in integral form as follows:

$$\int \frac{1}{py_2}dp = \int \frac{1}{(Z-1)\varphi_2}d\varphi_2 + \int \frac{(1-y_2)}{y_2(Z-1)\varphi_1}d\varphi_1 \tag{3}$$

In the preceding equations, $p$ is pressure, $y$ is the mole fraction of the species in the gas phase, $d$ is the derivative operator, $Z$ stands for the compressibility factor, $\varphi$ denotes the fugacity coefficient, and subscript 2 refers to triethylene glycol (solute). The properties $\varphi_1$, $\varphi_2$, and $Z$ can be calculated using a suitable thermodynamic model.

In eq 3, the left-hand side is designated by $A_\mathrm{P}$ and the right-hand side by $A_\varphi$, as follows:[3,17−31]

$$A_\mathrm{P} = \int \frac{1}{py_2}\mathrm{d}p \tag{4}$$

$$A_\varphi = A_{\varphi 1} + A_{\varphi 2} \tag{5}$$

$$A_{\varphi 1} = \int \frac{(1-y_2)}{y_2(Z-1)\varphi_1}\mathrm{d}\varphi_1 \tag{6}$$

$$A_{\varphi 2} = \int \frac{1}{(Z-1)\varphi_2}\mathrm{d}\varphi_2 \tag{7}$$

Thus, if a set of data is considered to be consistent, $A_\mathrm{P}$ should be equal to $A_\varphi$ within acceptable defined deviations. To set the margin of error, a percent area deviation ($\Delta A_i$ %) between experimental and calculated values is defined as:[3,17−31]

Table 1. Critical Properties and Acentric Factors of the Investigated Substances[41]

| sub.[a] | $T_c$/K[b] | $p_c$/MPa[c] | $\omega$[d] |
|---|---|---|---|
| methane | 190.56 | 4.599 | 0.01155 |
| $CO_2$ | 304.21 | 7.383 | 0.22362 |
| triethylene glycol | 769.50 | 3.320 | 0.75871 |

[a] Substance. [b] Critical temperature. [c] Critical pressure. [d] Acentric factor.

$$\Delta A_i\% = 100\left[\frac{A_{\varphi_i} - A_{\mathrm{P}_i}}{A_{\mathrm{P}_i}}\right] \tag{8}$$

where $i$ refers to the data set number. The maximum values accepted for these deviations regarding the proposed systems are evaluated using suitable mathematical procedures. The detailed derivations of the preceding equations can be found elsewhere.[3,17−31]

## 3. THERMODYNAMIC MODEL

Jerinić et al.[1] have previously demonstrated that the phase behavior of the mixtures of methane + triethylene glycol can be well-represented using the Soave−Redlich−Kwong (SRK) equation of state (EoS)[34] accompanied with van der Waals (vdW2) quadratic mixing rules.[35] Moreover, previous calculations[35,36] have shown that using a proper $\alpha$ function contributes to accurate phase behavior prediction/calculation results especially in supercritical fluid region. This is mainly because of the special shape of the $\alpha$ function versus critical temperature.[35,36] In this study, the well-known $\alpha$ function presented by Twu et al.[37,38] is applied for the SRK EoS.[34] Table 1 shows the physical properties of the investigated natural gas components.

## 4. METHODOLOGY

The data assessment test is performed through the following procedure:[3,17,18,24−31]

(1) Determine $A_\mathrm{P}$ from eq 4 using the experimental $p-T-y$ (pressure−temperature−molar composition of triethylene glycol in gas (solvent) phase) data. Use a numerical integration for this purpose. In this work, Simpson's 3/8 rule[39] has been applied.

(2) Evaluate $A_\varphi$ by eqs 5 to 7 using the obtained values for $\varphi_2$ and $Z$ from the thermodynamic model for the proposed system and $y_2$ from experimental data.

(3) For every set of the experimental data, determine an absolute percent area deviation ($\Delta A_i$%) between experimental ($A_\mathrm{P}$) and calculated values ($A_{\varphi i}$) using eq 8.

**4.1. Consistency Criteria.** The deviations of the thermodynamic model results should lie within a defined acceptable range. In this work, the accepted absolute relative deviations for the calculated mole fractions of triethylene glycol in the supercritical phase (defined by the following equation) are considered to be between (0 and 20) % according to the capabilities of the thermodynamic model for this purpose:[1,3,17,18,24−31]

$$\mathrm{ARD}\% = 100\frac{|y_i^{\mathrm{cal}} - y_i^{\mathrm{exp}}|}{y_i^{\mathrm{exp}}} \tag{9}$$

Table 2. Experimental Data[1,5,6] Ranges Used for Performing the Thermodynamic Assessment Test

| | | range of data | | | | |
|---|---|---|---|---|---|---|
| $S^a$ | set no. | $T$/K[b] | $N^c$ | $p$/MPa[d] | $y_2{}^e \cdot 10^7$ | ref[f] |
| $CH_4$ + TEG | 1 | 298.15 | 6 | 1.606−8.612 | 3.63−4.79 | 1 |
| $CH_4$ + TEG | 2 | 316.75 | 6 | 1.88−8.697 | 11−13.80 | 1 |
| $CO_2$ + TEG | 3 | 313.15 | 6 | 2.758−9.653 | 8.31−859.30 | 5,6 |
| $CO_2$ + TEG | 4 | 323.15 | 6 | 2.758−9.653 | 23.26−710.9 | 5,6 |
| $CO_2$ + TEG | 5 | 333.15 | 6 | 4.137−11.032 | 50.35−1373 | 5,6 |

[a] System. [b] Temperature. [c] Number of experimental data. [d] Pressur.e [e] Solubility of triethylene glycol, mole fraction. [f] Reference of experimental data.

where superscripts cal and exp refer to calculated and experimental values, respectively. It is shown that the ranges of ARD % of the model[1] results from experimental values[1,5] are generally acceptable for the data assessment test.

The error propagation has been performed on the existing experimental data to evaluate the acceptable percentages of deviations of the calculated areas from each other. This was done using the general equation of error propagation,[40] considering the temperature and mole fraction of triethylene glycol in gas phase as the independent measured variables.[3,17,18,24−31] The calculated individual area ($A_\varphi$) is the dependent variable of interest. The error in the calculated areas, $E_A$, and the percent error, $E_A$ %, are calculated as follows:[3,17,18,24−31]

$$E_A = \left[\frac{\partial A_{\varphi j}}{\partial T}\right]\Delta T + \left[\frac{\partial A_{\varphi j}}{\partial y}\right]\Delta y \tag{10}$$

$$E_A\% = 100\left[\left|\frac{E_A}{A_{\varphi j}}\right|\right] \tag{11}$$

where subscript $j$ refers to $j$th calculated area. We assume maximum uncertainties of 0.1 K for the experimental temperature and 5 % for the experimental solubility data.[1] However, these uncertainties depend on the method of experimental measurements, for example, the method used by Jerinić et al.[1] is based on the static method. The maximum acceptable errors are much more dependent on uncertainty of solubility measurements, and one can also neglect the first right-hand side term of eq 10.

The partial derivatives of the two preceding equations have been evaluated using the central finite difference[39] method. It results in a $\Delta A_i$ % between (0 and 23) %. Therefore, the range (0 to 23) % is established as the acceptable error range of thermodynamically consistent data calculated areas resulting from eqs 4 to 7.

The thermodynamic consistency test criteria are applied based on the steps presented in previous works.[3,17,18,24−31]

## 5. RESULTS AND DISCUSSION

Five experimental isothermal data sets[1,5,6] of solubilities of triethylene glycol in supercritical methane and carbon dioxide have been treated here for data assessment test. Table 2 summarizes the ranges of the corresponding data.

The results of calculations of the solubilities of triethylene glycol in supercritical methane and $CO_2$ have been shown in Table 3. The tuned binary interaction parameters using the applied thermodynamic model[1] are also reported in this table. It is implied that the applied model is able to represent the data of solubilities of triethylene glycol in supercritical methane within the acceptable absolute deviation range of (0 and 20) % requested for successful data assessment test. However, it is generally acceptable for the test on the solubility data of triethylene glycol in supercritical carbon dioxide after elimination of about 25 % of the results, that is, weak calculated values.

Table 3. Calculated Solubility of Triethylene Glycol in Supercritical Methane/Carbon Dioxide Using the Applied Thermodynamic Model[1]

| no.[a] | $T$/K | $p$/MPa | $y_2{}^{\mathrm{exp}\,b} \cdot 10^7$ | $y_2{}^{\mathrm{cal}\,c} \cdot 10^7$ | $k_{ij}{}^d$ | $l_{ij}{}^d$ | ARD[e] % |
|---|---|---|---|---|---|---|---|
| 1 | 298.15 | 1.606 | 3.63 | 3.50 | 0.353 | 0.010 | 3.6 |
| | | 3.243 | 2.87 | 2.73 | | | 4.9 |
| | | 5.132 | 3.05 | 2.91 | | | 4.6 |
| | | 6.485 | 3.45 | 3.34 | | | 3.2 |
| | | 7.485 | 4.1 | 3.81 | | | 7.1 |
| | | 8.612 | 4.79 | 4.47 | | | 6.7 |
| 2 | 316.75 | 1.88 | 13.80 | 16.00 | 0.454 | 0.099 | 15.9 |
| | | 3.313 | 11.30 | 12.00 | | | 6.2 |
| | | 4.903 | 11.00 | 11.10 | | | 0.9 |
| | | 6.392 | 11.10 | 11.10 | | | 0.0 |
| | | 7.505 | 11.70 | 11.60 | | | 0.9 |
| | | 8.697 | 12.20 | 12.40 | | | 1.6 |
| 3 | 313.15 | 2.758 | 8.31 | 10.53 | 0.137 | 0.086 | 26.8 |
| | | 4.137 | 13.7 | 13.68 | | | 0.1 |
| | | 5.516 | 27.2 | 23.82 | | | 12.4 |
| | | 6.895 | 115 | 59.64 | | | 48.1 |
| | | 8.274 | 358.9 | 360.83 | | | 0.5 |
| | | 9.653 | 859.3 | 1330.00 | | | 55.2 |
| 4 | 323.15 | 2.758 | 23.26 | 23.30 | 0.168 | 0.091 | 0.2 |
| | | 4.137 | 33.66 | 27.60 | | | 18.0 |
| | | 5.516 | 35.79 | 41.13 | | | 14.9 |
| | | 6.895 | 117.6 | 76.17 | | | 35.2 |
| | | 8.274 | 283.7 | 187.53 | | | 33.9 |
| | | 9.653 | 710.9 | 711.00 | | | 0.0 |
| 5 | 333.15 | 4.137 | 50.35 | 52.19 | 0.147 | 0.098 | 3.6 |
| | | 5.516 | 68.65 | 71.02 | | | 3.5 |
| | | 6.895 | 153.4 | 114.20 | | | 25.6 |
| | | 8.274 | 321.9 | 218.00 | | | 32.3 |
| | | 9.653 | 693 | 505.40 | | | 27.1 |
| | | 11.032 | 1373 | 1370.00 | | | 0.2 |

[a] Set number. [b] Mole fraction (experimental). [c] Mole fraction (calculated). [d] The orders of magnitude of the binary interaction parameters ($k_{ij}$ and $l_{ij}$) are in acceptable agreement with those reported by Jerinić et al.[1] [e] ARD% = $100((|y_2^{\mathrm{calc}} - y_2^{\mathrm{exp}}|)/y_2{}^{\mathrm{exp}})$. The superscripts exp and cal represent experimental and calculated values.

Table 4 reports the results of the thermodynamic consistency test for the investigated systems. It should be noted that the data points for which the proposed thermodynamic model does not lead to deviations within the acceptable range are ignored for the assessment test.

The results show that three of the studied experimental data sets that are well-calculated by the applied thermodynamic model[1] seem to be thermodynamically consistent and the other one seems not to be fully consistent. This fact may demonstrate the capability of the experimental procedure of measuring these solubilities in spite of several difficulties in such measurements. Another element inferred from the test results is that it seems that

Table 4. Detailed Results of Thermodynamic Data Assessment Test on the Investigated Experimental Data[1,5,6]

| no. | S[a] | T/K | p/MPa | Z[b] | $\varphi_1^{G}$[c] | $\varphi_2^{G}$[d] | $A_P$[e]·$10^6$ | $A_\varphi$[f]·$10^6$ | ΔA %[g] | test result |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $CH_4$ + TEG | 298.15 | 1.606 | 0.9732 | 0.9732 | 0.6979 | 4.79 | 4.67 | 2.5 | TC[h] |
| | | | 3.243 | 0.9474 | 0.9473 | 0.4834 | | | | |
| | | | 5.132 | 0.9199 | 0.9193 | 0.3174 | | | | |
| | | | 6.485 | 0.9023 | 0.9004 | 0.2361 | | | | |
| | | | 7.485 | 0.8906 | 0.8871 | 0.1906 | | | | |
| | | | 8.612 | 0.8788 | 0.8729 | 0.1506 | | | | |
| 2 | $CH_4$ + TEG | 316.75 | 1.88 | 0.9758 | 0.9757 | 0.7873 | 1.28 | 1.25 | 2.1 | TC |
| | | | 3.313 | 0.9588 | 0.9582 | 0.6606 | | | | |
| | | | 4.903 | 0.9415 | 0.9398 | 0.5483 | | | | |
| | | | 6.392 | 0.9272 | 0.9236 | 0.4651 | | | | |
| | | | 7.505 | 0.9177 | 0.9122 | 0.4143 | | | | |
| | | | 8.697 | 0.9089 | 0.9007 | 0.3689 | | | | |
| 4 | $CO_2$ + TEG | 323.15 | 2.758 | 0.8892 | 0.8983 | 0.3316 | 43.8 | 43.2 | 1.3 | TC |
| | | | 4.137 | 0.8274 | 0.8490 | 0.1761 | | | | |
| | | | 5.516 | 0.7593 | 0.8005 | 0.0862 | | | | |
| | | | 9.653 | 0.4875 | 0.6568 | 0.0033 | | | | |
| 5 | $CO_2$ + TEG | 333.15 | 4.137 | 0.8453 | 0.8643 | 0.1972 | 11.8 | 11.2 | 5.3 | NFC[i] |
| | | | 5.516 | 0.7866 | 0.8210 | 0.1036 | | | | |
| | | | 11.032 | 0.5058 | 0.6558 | 0.0027 | | | | |

[a] System. [b] Compressibility factor. [c] Fugacity coefficient of $CO_2/CH_4$ in gas phase. [d] Fugacity coefficient of triethylene glycol in gas phase. [e] Area of integral related to the experimental data. [f] Area of integral related to the calculated values. [g] Area deviation. [h] Thermodynamically consistent data. [i] Not fully consistent data.

these measurements have been done with careful calibration of the measuring devices like pressure transducers and temperature probes by the groups of the corresponding measurements.

Furthermore, the results of such a test introduce a procedure to select the experimental data by which a thermodynamic model is supposed to be tuned. Thermodynamically inconsistent data (sometimes not fully consistent data) used for tuning of the models may contribute to the inaccuracy in predictions of the model for further applications.[3,17,18,24−31]

## 6. CONCLUSION

In this study, a thermodynamic data assessment test was applied on the four isothermal experimental data sets[1,5,6] for the solubilities of triethylene glycol in supercritical methane and carbon dioxide. The SRK EoS[34] with vdW2 mixing rules[35] was used to calculate the corresponding solubilities. The data assessment test was based on the area test approach derived from the original Gibbs−Duhem equation[3,17−31] at a constant temperature.[3,17,18,24−31] The results showed that three data sets of the investigated experimental data of solubilities, which were well-represented by the applied model,[1] seem to be thermodynamically consistent, while the other one seems not to be fully consistent. In addition, the results indicated that the measurements of such data must be done accurately to be able to use in the tuning of the future models for predictions/representation of such solubilities in natural gas fluids. The presented test may leads to a better understanding of the importance of solubilities of hydrate inhibitors/dehydration agents in natural gas systems.

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