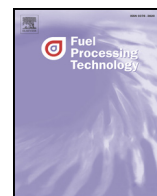




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## Assessment test for glycol loss in gaseous system

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### ABSTRACT

We herein apply a mathematical method for detection of the outliers in experimental phase equilibrium data of ethylene/triethylene glycol (EG/TEG) solubility in a gaseous system. Four Chrastil-type correlations including the original Chrastil, Adachi and Lu, del Valle and Aguilera, and Mèndez-Santiago and Teja are used to represent/predict the phase equilibria of the EG/TEG + carbon dioxide/methane systems. It is found that the employed correlations are statistically valid, one experimental solubility datum from the solubility data of the carbon dioxide + EG system might be doubtful, two data points may be referred to be the outliers evaluated by the Mèndez-Santiago and Teja correlation and one data point from the same dataset is found to be out of applicability domain of the Adachi and Lu and the Mèndez-Santiago and Teja correlations.

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### 1. Introduction

The presence of water in the natural gas processes (even negligible or non-negligible amounts) is of great concern for the petroleum industry [1–5]. Formation of gas hydrates (gas hydrates are inclusion compounds composed of H<sub>2</sub>O and guest species [1]) and water condensates that eventually lead to corrosion of the processing facilities and excess pressure drop in pipelines are just a few issues originating from the existence of water in the corresponding processes. Therefore, glycols (mostly triethylene glycol or TEG) are normally injected to the wet gas flows in dehydration units to absorb the gas humidity and adjust the water dew-point temperature [1–10].

However, the experimental evidences [6–9] show that non-negligible glycol quantities may be dissolved in the gas stream, which can be considered as glycol loss of the dehydration process [1,5,6]. Higher gas processing costs as well as a considerable pressure drop of the gas flow due to probable retrograde condensation of triethylene glycol in pipelines may be significant consequences of the glycol vaporization loss [7].

In order to design efficient gas dehydration processes, reliable experimental solubility data of glycol loss in the vapor phase are required. In spite of the fact that the experimental methane and carbon dioxide

solubility data in aqueous ethylene/triethylene glycols have been extensively reported in the literature, solubility data of EG and TEG in supercritical methane and carbon dioxide [6,8] seem to be scarce [4,5]. On the other hand, high experimental uncertainties resulting from inaccurate calibration of pressure transducers, temperature probes, and/or detectors of gas chromatographs, probable errors in measurements of phase equilibria (particularly at low concentrations of the species) [11,12], improper design of the equipment and so forth may result in high uncertainty of the available data [4,5].

In a previous work [5], the experimental data of solubility of TEG in supercritical CO<sub>2</sub> and methane was assessed to check their thermodynamic consistency. Thus, it is of interest to pursue another approach on the basis of a statistically-correct method [13–15] for simultaneous detection of the doubtful data and their quality along with checking the validity and domain of applicability of the existing correlations in the literature for their representation. The quality of the phase equilibrium data of the EG + CO<sub>2</sub> system is also checked in this work.

### 2. Theory

#### 2.1. Hat matrix and Williams plot

Detection (or diagnostics) of the outliers may be of significance in developing the mathematical models, as described in our previous works [16,17], due to identification of individual datum (or groups of

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data) that may differ from the bulk of the data present in a dataset [13–17]. The Leverage approach [13–15], which is applied in the present study, includes numerical + graphical steps [16,17]. The calculation procedure of this method consists of determination of the residual values (i.e. the deviations of a model's results from the experimental data) and a matrix known as Hat matrix composed of the experimental data and the calculated values obtained from a correlation (model) [13–17]. An appropriate mathematical model is therefore needed to employ the aforementioned strategy [13–17].

The following relation is generally used to form the Hat matrix (H) and its indices [13–17]:

$$H = X(X^tX)^{-1}X^t \quad (1)$$

where X is a two-dimensional matrix composing *n* data (rows) and *k* parameters (of the model) (columns) and *t* stands for the transpose matrix. The Hat values in the feasible region of the problem are the diagonal elements of the Hat matrix [13–17].

The graphical detection of the suspended (doubtful) data or outliers is undertaken through sketching the Williams plot on the basis of the calculated H values through Eq. (1). This plot shows a correlation between the Hat indices and standardized cross-validated residuals (SR), which are defined as the difference between the represented values and the implemented data [15–17]. A warning Leverage ( $H^*$ ) is applied to identify the applicability domain of the model (correlation), which is normally equal to  $3p/n$ , where *n* is number of training points (represented data) and *p* is the number of model (correlation) input parameters plus one [15–17]. The leverage of 3 is generally considered as a “cut-off” value to define the points within  $\pm 3$  range (two horizontal red lines) standard deviations from the mean (to cover 99% normally distributed data) [15–17]. Existence of the majority of data points in the ranges  $0 \leq H \leq H^*$  and  $-3 \leq R \leq 3$  reveals that the applied models exhibit wide applicability domains. In addition, it contributes to this conclusion that the model is a statistically valid one [13–17]. “Good High Leverage” points are located in the domain of  $H^* \leq H$  and  $-3 \leq R \leq 3$ . These points can be designated as the ones, which are outside of applicability domains of the applied models [15–17]. In other words, the model is not able to represent or predict the following data. The points located in the range of  $R < -3$  or  $3 < R$  (whether they are larger or smaller than the  $H^*$  value) are designated as outliers of the model or “Bad High Leverage” points. These inaccurate representations/predictions may be attributed to the doubtful data [15–17].

## 2.2. Chrastil-type correlations

We have used four previously recommended [4] Chrastil-type correlations [18,20–22] to calculate the solubility of EG/TEG in CO<sub>2</sub>/methane.

### 2.2.1. Chrastil correlation

The original Chrastil correlation [18] was developed with the assumption that the solute molecules associated with the gas (solvent) molecules are in chemical equilibrium with the resulting complex (solvate complex) that can be expressed as follows [4,18,19]:



where *k* stands for the association term, *A'* is the solute molecule, and *B'* represents the gas (solvent) molecule. The equilibrium concentration of the solute is calculated as follows [4,18,19]:

$$c/\text{g dm}^{-3} = (\rho/\text{g dm}^{-3})^k \exp\left(\frac{a}{T/K} + b\right). \quad (3)$$

In Eq. (3), *c* is the concentration of a solute in a gas,  $\rho$  denotes the density of the gas (solvent), *T* is temperature, and *a* and *b* are the adjustable parameters of the equation, respectively.

### 2.2.2. Adachi and Lu correlation

The following equation has been recommended by Adachi and Lu [20], in which the association term (*k*) in Eq. (3) can be expressed as a function of gas (solvent) density as follows [22]:

$$k = e_1 + e_2\rho + e_3\rho^2 \quad (4)$$

where  $e_{1-3}$  are adjustable parameters.

### 2.2.3. del Valle and Aguilera correlation

The following equation has been developed by del Valle and Aguilera [21] to determine low solubilities of solutes in supercritical gases:

$$c/\text{g dm}^{-3} = (\rho/\text{g dm}^{-3})^k \exp\left(a + \frac{b}{T/K} + \frac{d}{(T/K)^2}\right) \quad (5)$$

where *a*, *b*, and *d* are the adjustable parameters determined for a system of interest.

### 2.2.4. Mèndez-Santiago and Teja correlation

Mèndez-Santiago and Teja [22] proposed Eq. (6) considering the direct effects of pressure on the solubilities of different solids in gases:

$$y/\text{mole fraction} = \frac{1}{P/\text{MPa}} \exp\left(\frac{a}{T/K} + \frac{b \cdot \rho/(\text{mol ml}^{-1})}{T/K} + d\right) \quad (6)$$

where *y* denotes the solubility of solute, *P* is the pressure, and *a*, *b*, and *d* are the three adjustable parameters of the equation.

## 3. Experimental data

The existing experimental solubility data of EG/TEG in CO<sub>2</sub>/methane [6,8] have been herein evaluated. Table 1 reports the ranges of the experimental data.

## 4. Results and discussion

It has been already demonstrated that the applied correlations lead to generally acceptable results for representation of the phase equilibrium data of the EG/TEG + supercritical CO<sub>2</sub>/methane systems [4]. The critical properties, and acentric factors of the investigated compounds as well as recommended parameters of the correlations are reported in Table 2 and Tables 3–6 respectively.

To achieve our objectives, the H values have been calculated using Eq. (1) and the Williams plots have been sketched in Figs. 1 to 12. The calculated H and *R* values accompanied with the average absolute relative deviations of the correlations results from the experimental values [6,8] are presented in Table 7. The warning Leverages ( $H^*$ ) have been fixed at  $3p/n$  for the whole datasets. Furthermore, the

**Table 1**  
Experimental data [6,8] ranges of solubility of glycols in supercritical gases evaluated in this work.

Sys. <sup>a</sup>	N <sup>b</sup>	RE <sup>c</sup>		
		T <sup>d</sup> /K	P <sup>e</sup> /MPa	y/mole fraction × 10 <sup>6f</sup>
CH <sub>4</sub> + TEG	12	298.15–316.75	1.606–8.697	0.287–1.38
CO <sub>2</sub> + TEG	9	323.15–323.15	2.758–11.032	2.33–137
CO <sub>2</sub> + EG	36	308.15–333.15	2.76–22.06	33.4–5640

<sup>a</sup> System.

<sup>b</sup> Number of data points.

<sup>c</sup> Range of experimental solubility data.

<sup>d</sup> Temperature.

<sup>e</sup> Pressure.

<sup>f</sup> Glycol solubility.

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