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A statistical method for evaluation of the experimental phase equilibrium data of simple clathrate hydrates

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H I G H L I G H T S

- ▶ Leverage method is applied for evaluation of experimental phase equilibrium data.
- ▶ Experimental phase equilibrium data of various simple clathrate hydrates are studied.
- ▶ 5 hydrate dissociation data are found to be probable doubtful ones.
- ▶ 10 data points are designated as out of applicability domain of the correlation.

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We, herein, present a statistical method for diagnostics of the outliers in phase equilibrium data (dissociation data) of simple clathrate hydrates. The applied algorithm is performed on the basis of the Leverage mathematical approach, in which the statistical Hat matrix, Williams Plot, and the residuals of a selected correlation results lead to define the probable outliers. This method not only contributes to outliers diagnostics but also identifies the range of applicability of the applied model and quality of the existing experimental data. The available correlation in the literature in exponential form is used to represent/predict the hydrate dissociation pressures for three-phase equilibrium conditions (liquid water/ice–vapor–hydrate). The investigated hydrate formers are methane, ethane, propane, carbon dioxide, nitrogen, and hydrogen sulfide. It is interpreted from the obtained results that the applied correlation for calculation/estimation of the phase behavior of simple clathrate hydrate systems is statistically valid and correct, 5 hydrate dissociation data are found to be probable doubtful ones and 10 data points are out of applicability domain of the applied correlation.

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1. Introduction

Clathrate (gas) hydrates are inclusion compounds composed of H₂O and guest species (Sloan and Koh, 2008). They are normally stabilized by the guest molecules (can be either gas or special liquids) enclathrated in the hydrogen-bonded water cages. At relatively high pressures and low temperatures, water molecules form various crystalline structures generally depending on the size and shape of the guest molecule(s) (Sloan and Koh, 2008). Structures I (sI), II (sII), and H (sH) are known to form as three common structures of clathrate hydrates.

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The first industrial importance of the gas hydrate formation has been attributed to the blockage of gas/oil transportation lines in petroleum industry in the early 1930s (Sloan and Koh, 2008; Hammerschmidt, 1934). More rigorously, gas hydrate formation may occur during the steps of production and processing of natural gas when traceable amounts of associated water exist (even in the form of very low water content). Furthermore, novel technologies utilizing gas hydrates have attracted much attention in the recent years (called positive applications) (Sloan and Koh, 2008; Eslamimanesh et al., 2012a). For instance, these clathrate structures may be used as media for the storage and transportation of natural gas and hydrogen (Sloan and Koh, 2008; Eslamimanesh et al., 2012a).

With respect to the aforementioned points, accurate and reliable phase equilibrium data are required to design the most efficient processes (either to prevent gas hydrate formation or to use it as a promising technique for other applications) and to adjust the parameters of the developed models (thermodynamic/numerical ones) for the corresponding phase equilibrium calculation/prediction.

Experimental phase equilibrium data (mainly dissociation data) for simple clathrate hydrate systems e.g. CH₄, C₂H₆, C₃H₈, CO₂, N₂, H₂S, etc. have been extensively reported in the literature (Sloan and Koh, 2008). Different experimental techniques have been thus far applied for obtaining these data (Sloan and Koh, 2008; Eslamimanesh et al., 2012a).

Although the quantities of these reported data seem to be adequate for industrial applications, there may be no general method to check their qualities. However, two methods have been already employed to check the reliability of phase equilibrium data of the systems containing gas hydrates as follows:

- (1) The sketch of logarithm of dissociation pressure ($\log(p)$) vs. reciprocal temperature ($1/T$) generally exhibits a straight line (which shows the value of the enthalpy of hydrate formation). Thus, the hydrate dissociation data for any of the simple hydrate formers can be sketched to observe whether they show the same trends or not (Eslamimanesh et al., 2011a).
- (2) Thermodynamic consistency test is generally applied as a reliable method for assessment of the phase equilibrium data quality. Very recently, we performed consistency test method for the first time on significant systems including water content of methane in equilibrium with gas hydrate, liquid water or ice, (Eslamimanesh et al., 2011b), solubility data of carbon dioxide and methane with water inside and outside gas hydrate formation region, (Eslamimanesh et al., 2011c) and composition of vapor phase in equilibrium with gas hydrate and liquid water for the carbon dioxide+methane or nitrogen+water systems (Eslamimanesh et al., 2012b). However, the preceding method is generally applicable only in the case of applicability of molar compositions of equilibrium phases. It is worth pointing out that the studied phase equilibrium data include the molar compositions of the phases which are not necessarily the hydrate dissociation conditions. Such data are very scarce in the open literature. As a consequence, this method may not be an efficient technique of our concern in this work (Belandria et al., 2011).

Hence, it is of much interest to propose a statistically-correct method for simultaneous detection of the doubtful data and their quality along with checking the validity and domain of applicability of an available correlation (in exponential form) for representation/prediction of the phase equilibrium data of simple clathrate hydrates. In the present study, we use the Leverage approach (Rousseeuw and Leroy, 1987; Goodall, 1993; Gramatica, 2007) for this purpose. To the best of our knowledge, this is the first time that a statistical method is used for evaluation of such data.

2. Theory

2.1. Leverage approach

As mentioned in our previous work, outlier diagnostics (or detection) may be crucial in developing the mathematical models (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012). Outlier detection is to identify individual datum (or groups of data) that may differ from the bulk of the data present in a dataset (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012). The proposed methods for this purpose normally consist of numerical and graphical algorithms (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012). One of the efficient and reliable statistical algorithm for outlier diagnostics is the Leverage approach (Rousseeuw and Leroy, 1987; Goodall, 1993; Gramatica, 2007). The employed elements of this method includes the values of the residuals (i.e. the deviations of a model results from the experimental data) and

a matrix known as Hat matrix composed of the experimental data and the represented/predicted values obtained from a correlation (model) (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012). Hence, a suitable mathematical model is also required to pursue the calculation steps of the algorithm.

The Leverage or Hat indices are determined as a Hat matrix (H) with the following definition (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012; Gharagheizi et al., 2012):

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

where X is a two-dimensional matrix composing n chemicals or data (rows) and k parameters of the model (columns) and t stands for the transpose matrix. The Hat values of the chemicals in the feasible region of the problem are, as a matter of fact, the diagonal elements of the H matrix.

The Williams plot is later sketched for graphical identification of the suspended data or outliers on the basis of the calculated H values through Eq. (1). This plot shows the correlation of Hat indices and standardized cross-validated residuals (R), which are defined as the difference between the represented/predicted values and the implemented data (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012; Gharagheizi et al., 2012). A warning Leverage (H) is generally fixed at the value equal to $3n/p$, where n is number of training points and p is the number of model (correlation) input parameters plus one (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012; Gharagheizi et al., 2012). The leverage of 3 is normally considered as a “cut-off” value to accept the points within ± 3 range (two horizontal red lines) standard deviations from the mean (to cover 99% normally distributed data) (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012; Gharagheizi et al., 2012). Existence of the majority of data points in the ranges $0 \leq H \leq H^*$ and $-3 \leq R \leq 3$ reveals that both model development and its representations/predictions are done in applicability domain, which results in a statistically valid model. “Good High Leverage” points are located in domain of $H^* \leq H$ and $-3 \leq R \leq 3$. The Good High Leverage can be designated as the ones, which are outside of applicability domain of the applied model (Rousseeuw and Leroy, 1987; Goodall, 1993; Mohammadi et al., 2012; Gharagheizi et al., 2012). In other words, the model is not able to represent/predict the following data at all. 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 erroneous representations/predictions can be attributed to the doubtful data (Rousseeuw and Leroy, 1987; Goodall, 1993; Gharagheizi et al., 2012).

2.2. Correlation

As the Leverage approach (Rousseeuw and Leroy, 1987; Goodall, 1993; Gramatica, 2007) seems to have been developed for checking the applicability domain of the models merely based on the numerical regressions, we have used the following recommended simple correlation to represent/predict the corresponding phase equilibrium data (Sloan and Koh, 2008; Kamath, 1984)

$$p/MPa = 10^{-3} \exp(a + b.T^{-1}/K) \quad (2)$$

where p stands for the dissociation pressure, T is the dissociation temperature, and a and b are the parameters of the correlation, which are reported in Table 1. (Sloan and Koh, 2008; Kamath, 1984). It should be noted that the range of dissociation temperatures and the phase equilibrium regions, for which Eq. (2) has been recommended are also presented in Table 1 (Sloan and Koh, 2008; Kamath, 1984).

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