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Phase Equilibrium Modeling of Structure H Clathrate Hydrates of Methane + Water “Insoluble” Hydrocarbon Promoter Using Group Contribution-Support Vector Machine Technique

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 Supporting Information

ABSTRACT: In this work, the group contribution (GC) method is coupled with the least-squares support vector machine (LSSVM) mathematical algorithm to develop a model for representation/prediction of the dissociation conditions of structure H (sH) clathrate hydrates of methane with 21 hydrocarbon promoters namely as water “insoluble” promoters. Almost all of available literature data are studied to present a reliable model validated by the following statistical parameters: absolute average relative deviations (AARD) of the represented/predicted dissociation pressures from the reported experimental values: about 1.6%, and squared correlation coefficient: 0.99.

1. INTRODUCTION

Gas hydrates or clathrate hydrates are crystalline solid compounds composed of water and small gas molecules, such as CO₂, N₂, CH₄, H₂, etc., under suitable conditions of low temperatures and specified pressures.^{1–3} They are a subset of compounds known as clathrates (come from the Greek word “khlatron”) or inclusion compounds.^{1,2} A clathrate compound is one, in which a molecule or molecules of one or several components (guest molecules) are enclosed in a structure built from molecules of another component (host molecules).^{1,2} The majority of gas hydrates are known to form three typical hydrate crystal structures: structure I (sI), structure II (sII), and structure H (sH).^{1,2} The type of crystal structure generally depends on the size of the guest molecule(s).^{1,2}

Formation of gas hydrates was found to be one of the reasons of transportation pipelines blockage in natural gas industry in early 1930s.^{1,2,4} However, many positive applications of clathrate hydrates, for example, in CO₂ capture and sequestration, gas storage, air-conditioning systems in the form of hydrate slurry, water desalination and treatment technology, concentration of dilute aqueous solutions, separation of different gases from flue gas streams, etc., have been reported, especially in the recent years.^{5–9}

Many investigations argue that the gas hydrate structures have considerable potential for storage of special gases, for example, they have been proposed for natural gas and hydrogen storage and transportation,^{10–37} as cool storage media in air conditioning systems etc.^{38–41} However, slow gas hydrate formation rates

and high pressure or low temperature conditions for industrial applications of clathrate hydrate storage processes are among the factors, which have been subjects of many studies in recent years. Gas hydrate promoters are normally added to the hydrate crystallization (formation) processes to reduce the required hydrate formation pressure and increase the formation rate and/or temperature along with probable modification of the selectivity of hydrate cages for absorption of various gas molecules in the water cages or increase the storage capacity of these structures.⁴²

In a previous work,⁴² we argued that there is still a need to develop more accurate and predictive models for investigation of the phase equilibrium of such systems and consequently developed two molecular approaches using the quantitative structure–property relationship (QSPR) algorithm. In this communication, the group contribution (GC) method is coupled with the least-squares support vector machine (LSSVM)⁴³ mathematical tool to propose a novel approach for determination of the dissociation conditions of structure H clathrate hydrates of the methane + hydrocarbon promoter system namely as water “insoluble” promoters. The GC algorithm divides a molecule into small parts (generally named as “segments”). Each of these segments is considered as a functional group and has a contribution to the

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physicochemical properties of the specified molecule. Finally, the value of the property is defined through calculating the summation of the contributions of all functional groups in a molecule.

The present study is a continuation of the series of our efforts to develop predictive tools for determination of the physicochemical properties of pure organic compounds or mixtures applying various algorithms.

2. EXPERIMENTAL DATA AND MATHEMATICAL ALGORITHMS

2.1. Experimental Database. The reliability of models normally depends on the validity of the applied data set for their development.^{42–49} In this work, we tried to use almost all of the experimental data regarding the hydrate phase equilibrium of system of water insoluble hydrocarbon promoter + methane + water available in open literature.^{50–66} The chemical structures and other information about the investigated clathrate hydrate promoters (21 promoters) are reported in Table 1 in the Supporting Information file.

2.2. Determination of New Group Contributions. Having defined the data set, the chemical structures of all of the studied compounds have been analyzed with much attention using a mathematical algorithm comparing the chemical groups to define the most efficient contributions for evaluation of the corresponding phase equilibria. Consequently, 13 functional groups have been found to be more efficient for this purpose. The functional groups used in this study are presented in Table 2 in the Supporting Information file.

2.3. Optimization of the Parameters Using Support Vector Machine. The most significant calculation step is to search for a relationship between the chemical functional groups and the desired results, in which we are interested.^{42–49} The simplest method for this purpose is to assume a multilinear relationship between these groups and the desired parameter (here the hydrate dissociation pressure). This method is a similar technique employed in most of classical group contribution methods. Several calculations show that application of the mentioned methodology for the current problem does not lead to obtain accurate results within acceptable range of the deviations from experimental values.^{50–66} Hence, a nonlinear algorithm may solve the problem. Our computational results demonstrated that a powerful mathematical approach should be used for this purpose.

Although the artificial neural networks (ANN)-based models have been generally proven to provide high accuracy,^{42–49} they may have the disadvantages of nonreproducibility of results, partly as a result of random initialization of the networks and variation of the stopping criteria during optimization.^{67–70} The support vector machine (SVM) is a famous strategy developed from the machine-learning community.^{67–70} The advantages of the SVM methods in comparison with the traditional ANNs are generally as follows:^{43,67–72}

1. More probability for convergence to the global optimum
2. Normally find a solution that can be quickly obtained by a standard algorithm (quadratic programming)
3. Need not to determine the network topology in advance; which can be automatically determined as the training process ends
4. There is generally less probability of the SVM strategy to be faced with overfitting or under-fitting problem due to less number of parameters required for its development than the ANN methods.

The SVM outstanding performance makes it to be superior to most of the traditional empirical risk minimization principles. Furthermore, as a result of their specific formulation, sparse solutions can be found and both linear and nonlinear regression can be performed.^{43,67–72} A brief description of the SVM formulation is presented in the Supporting Information.^{43,90–93}

However, Suykens and Vandewalle⁷² have considered a modification to the original SVM⁴³ to overcome the difficulty of the previous algorithm in finding the final solution because it requires the solution of a set of nonlinear equations (quadratic programming). Their method, named as least-squares support vector machine (LSSVM),⁷² encompasses advantages similar to those of SVM,⁴³ but it requires solving a set of only linear equations (linear programming), which is much easier and more rapid compared to the traditional SVM method.^{42,43,67–72}

The regression error of the LSSVM⁷² approach is defined as the difference between the represented and predicted property values and experimental ones, which is considered as an addition to the constraint of the optimization problem. In traditional SVM method,⁴³ the value of the regression error is generally optimized during the calculations while in the LSSVM,⁷² the error is mathematically defined.^{42,43,67–72}

The cost function (penalized cost function, Q_{LSSVM}) of the applied⁷² method has been defined as^{42,43,67–72}

$$Q_{\text{LSSVM}} = \frac{1}{2} w^T w + \gamma \sum_{k=1}^N e_k^2 \quad (1)$$

subject to the following constraint:

$$y_k = w^T \varphi(x_k) + b + e_k \quad k = 1, 2, \dots, N \quad (2)$$

In the two preceding equations, x is the input vector of parameters of the model (group contributions), y denotes the outputs (dependent parameter), b is the intercept of the linear regression in the modified SVM method (LSSVM),⁷² w is the regression weight (slope of the linear regression), e_k stands for the regression error for N training objects (the least-squares error approach), γ indicates the relative weight of the summation of the regression errors compared to the regression weight (first right-hand side of eq 1), φ is the feature map, mapping the feasible region (input space) to a high dimensional feature space, and superscript T denotes the transpose matrix.

Using the Lagrange function,^{43,67–72} the weight coefficient (w) is written as^{42,43,67–72}

$$w = \sum_{k=1}^N \alpha_k x_k \quad (3)$$

where

$$\alpha_k = 2\gamma e_k \quad (4)$$

Assuming the linear regression between the independent and dependent variables of the LSSVM algorithm, eq 2 is rewritten as^{42,43,67–72}

$$y = \sum_{k=1}^N \alpha_k x_k^T x + b \quad (5)$$

Therefore, the Lagrange multipliers are calculated as^{42,43,67–72}

$$\alpha_k = \frac{(y_k - b)}{x_k^T x + (2\gamma)^{-1}} \quad (6)$$

The aforementioned linear regression can be well extended to nonlinear one using the Kernel function as^{42,43,67–72}

$$f(x) = \sum_{k=1}^N a_k K(x, x_k) + b \quad (7)$$

where $K(x, x_k)$ is the Kernel function calculated from the inner product of the two vectors x and x_k in the feasible region built by the inner product of the vectors $\Phi(x)$ and $\Phi(x_k)$ as follows:^{42,43,67–72}

$$K(x, x_k) = \Phi(x)^T \cdot \Phi(x_k) \quad (8)$$

In this work, the radial basis function (RBF) Kernel has been applied as shown below^{42,43,67–72}

$$K(x, x_k) = \exp(-||x_k - x||^2/\sigma^2) \quad (9)$$

where σ is considered to be a decision variable, which is optimized by an external optimization algorithm during the calculations. The mean square error (MSE) of the results of the LSSVM⁷² algorithm has been defined as

$$MSE = \frac{\sum_{i=1}^n (P_{rep/pred,i} - P_{exp,i})^2}{ns} \quad (10)$$

where p is the hydrate dissociation pressure, subscripts rep/pred and exp indicate the represented/predicted and experimental hydrate dissociation pressure values, respectively, and ns is the number of samples from the initial population. In this study, we have used the LSSVM⁷² algorithm developed by Pelckmans et al.⁷³ and Suykens and Vandewalle⁷² with some modifications, which will be discussed later.

Because we face with a range of equilibrium pressure values for different systems, these values have been normalized between -1 and $+1$ to prevent truncation errors.⁴⁴ This can be performed using maximum and minimum numbers of each functional group present in each promoter or input data and using maximum and minimum values of equilibrium pressure for output parameters. In addition, this procedure, which is done in optimization process, is performed to obtain the parameters of the LSSVM⁷² algorithm (γ and σ^2) and it has no effects on the model results. Later, these values are again changed to the original equilibrium pressures, which are finally used as the inputs and reported as outputs of the developed model. In the next step, the database is divided into three subdata sets including the “Training” set, the “Optimization” set, and the “Test” set. In this study, the “Training” set is used to generate the model structure, the “Optimization” set is applied for optimization of the model, and the “Test (prediction)” set is used to investigate the prediction capability and validity of the proposed model. The division of database into three subdata sets is normally performed randomly. For this purpose, about 80%, 10%, and 10% of the main data set are randomly selected for the “Training” set (240 data points), the “Optimization” set (29 data points), and the “Test” set (29 data points). The effect of the percent allocation of the three subdata sets from the database on the accuracy of the final model has been studied elsewhere.⁷⁴ In distribution of the data through the three subdata sets, we generally perform many distributions to avoid the local accumulations of the data in the feasible region of the

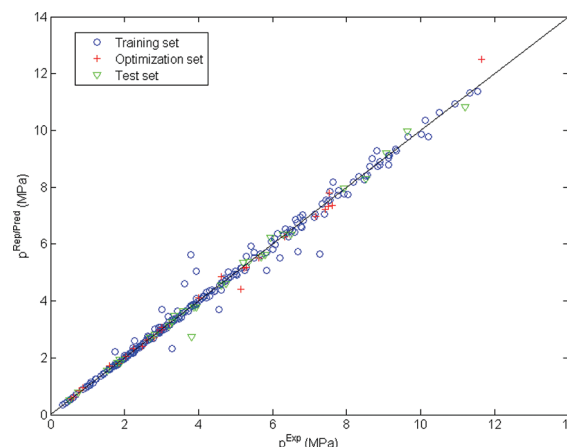


Figure 1. Comparison between the represented/predicted results of the first developed GC-LSSVM and experimental values^{50–66} of hydrate dissociation conditions of the investigated systems. p : Pressure.

problem. As a result, the acceptable distribution is the one with homogeneous accumulations of the data on the domain of the three subdata sets.

3. RESULTS AND DISCUSSION

The group contributions have been treated using the LSSVM⁷² mathematical method to develop an accurate and reliable model. The two main parameters of this algorithm are σ^2 and γ , which are supposed to be optimized using a proper optimization method. However, selecting the best optimization algorithm for this purpose is still a challenge. To select the most efficient one, the following characteristics of the corresponding algorithm should be taken into account:^{67,75–83}

1. Ability to handle nondifferentiable, nonlinear, and multi-modal cost functions
2. No requirement of extensive problem formulation while in traditional methods (such as integer programming, geometric programming, branch and bound methods etc.) special mathematical formulation is necessary for solving a problem
3. Ease of use, that is, few control variables to steer the minimization. These variables should also be robust and easy to choose
4. No sensitivity to starting point
5. Good convergence properties, that is, consistent convergence to the global optimum in consecutive independent trials.

Because of the preceding factors, application of nonpopulation based optimization methods, such as simplex simulated annealing algorithm (M-SIMPASA),⁸⁴ and Levenberg–Marquardt (LM)⁸⁵ may be erroneous.^{42,67}

In this work, we have modified the optimization part of the LSSVM⁷² algorithm developed by Pelckmans et al.⁷³ and Suykens and Vandewalle⁷² to use the robust hybrid genetic algorithm (H-GA) method.^{77–79} This modification not only results in more quick computational steps but also no sensitivity to starting points in which we are interested. For this purpose, the traditional genetic algorithm⁸⁶ has been hybridized with pattern-search method to perform the local optimization more accurate and faster than the traditional genetic algorithm method.⁸⁶ Therefore, the optimization toolbox of MATLAB software has been implemented, which is able to perform parallel computations.

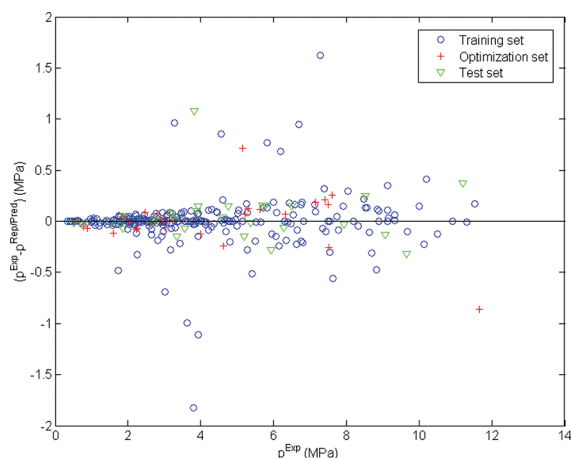


Figure 2. Deviations of the determined hydrate dissociation pressure values of the studied systems by the first developed model from experimental values.^{50–66}

This feature may effectively decrease the required time of the optimization to converge to the global optimum. The number of populations of the optimization algorithm applied in this work was set to 1000. To ensure that the global optimum has been obtained, the optimization procedure was repeated for several times.

The determined hydrate dissociation conditions and their absolute deviations using this method (first model) in comparison with the experimental values,^{50–66} are indicated in Figures 1 and 2. It has been found that the squared correlation coefficients, absolute average deviations, standard deviation errors, and root-mean-square errors of the developed model over the “Training” set, the “Optimization” set, the “Test (Prediction)” set, and the main data set for the GC-LSSVM model are 0.990, 0.992, 0.992, 0.990, 2.7%, 6.3%, 6.1%, 2.8%, 0.26, 0.24, 0.24, 0.06, 0.26, 0.24, 0.25, and 0.25, respectively.

Careful scrutiny of the obtained results shows that there are 16 data points, for which the presented model results lead to more than 8.8% absolute deviations from experimental values^{50–66} (based on Figures 1 and 2). Because these points do not belong to particular group of hydrocarbon promoters, we may suspect that corresponding experimental data are not accurate or may be somehow erroneous because of the existing difficulties in such experimental measurements (and we may not be able to conclude that the developed model has drawback in representation or prediction of hydrate dissociation conditions of particular types of promoters). The lower bound (8.8%) for the AAD of the results to be recognized as probable outliers of the model has been selected based on the fact that after this value, the deviations of the results begin to increase rapidly (with a sharp slope). For further investigation of the reliability of such data, we have pursued the following procedure:

1. Eliminating the outlier data points (16 points) from the investigated experimental values.^{50–66}
2. Developing a new GC-LSSVM model for representation/prediction of the remaining equilibrium pressure values (282 points).
3. Prediction of the eliminated outlier values using the new developed model for further checking the reliability of these values.

The results of the new developed model are shown in Figure 3. More detailed results including the absolute deviation ranges of

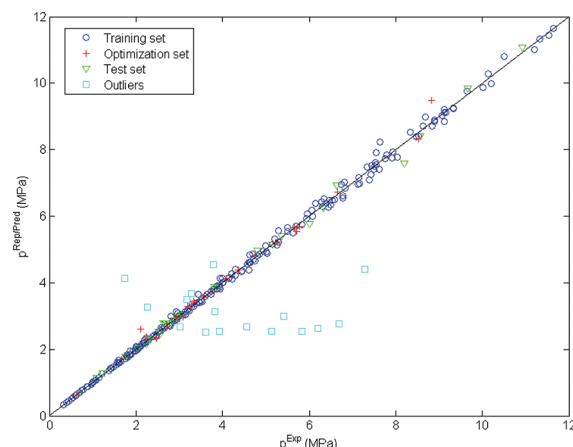


Figure 3. Comparison between the represented/predicted results of the final developed GC-LSSVM and experimental values^{50–66} of hydrate dissociation conditions of the investigated systems.

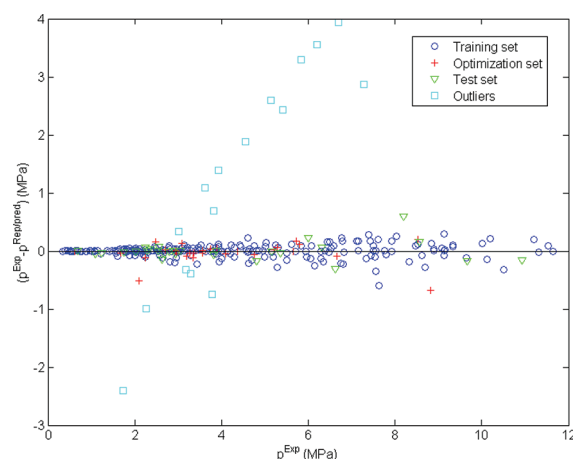


Figure 4. Deviations of the determined hydrate dissociation pressure values of the studied systems by the final developed model from experimental values.^{50–66}

the represented and predicted hydrate dissociation pressure values using the first and the second models are reported in Figure 4. Furthermore, the statistical parameters of both of the models are reported in Table 1. The average absolute deviation of the model is about 1.6% while this value is about 2.8% regarding the previous model results. All of the determined pressure values by the presented GC-LSSVM model, the corresponding deviations from experimental values,^{50–66} and the detailed allocation of the functional groups in each organic promoter are extensively presented Table 3 in the Supporting Information file. It is inferred from these results that all of the calculated or predicted hydrate dissociation pressure values for outlier (eliminated) data points bring about high deviations (over 8.8%) even in the new developed model. Therefore, it can be implied that these data points may be among the probable doubtful data with higher experimental uncertainties, as we have already expected from the first model results. The *mat* file (MATLAB file format) of the new obtained group contribution method containing all the parameters of the model is freely available upon request to the authors. A detailed example is presented in Appendix to show how the model (and the corresponding computer program) can

Table 1. Statistical Parameters of the Two Proposed GC-LSSVM Models

statistical parameter	value	
	first model	second model
training set		
R^{2a}	0.990	1.000
absolute average relative deviation, ^b %	2.7	1.5
standard deviation error	0.26	0.10
root mean square error	0.26	0.10
N^c	240	226
optimization set		
R^{2a}	0.992	0.990
absolute average relative deviation, ^b %	6.3	5.5
standard deviation error	0.24	0.18
root mean square error	0.24	0.18
N^c	29	28
test set		
R^{2a}	0.992	1.000
absolute average relative deviation, ^b %	6.1	4.0
standard deviation error	0.25	0.16
root mean square error	0.25	0.15
N^c	29	28
training + optimization + test set		
R^{2a}	0.990	1.000
absolute average relative deviation, ^b %	2.8	1.6
standard deviation error	0.06	0.03
root mean square error	0.25	0.12
N^c	298	282

^a R^2 : Squared correlation coefficient. ^b % AARD = $(100/N - n) \sum_i^N (|Rep(i)/Pred(i) - Exp(i)|/Exp(i))$, where n is the number of the model parameters. ^c Number of experimental data.

be used to calculate and estimate the hydrate dissociation pressure values for a particular system.

The results of a particular computational route to achieve the optimum parameters of the LSSVM⁷² model are shown in Figure 5. The value of the probable global optimum of the problem (although determination of the real global optimum of the problem may not be generally easy), that is, a compromise between all of the local optima can be well-interpreted in the figure. Large difference between the values of the LSSVM⁷² parameters leads us not be able to show all of the local optimums of the problem during the optimization procedure. However, it is possible to observe these values by scaling-up the presented figure. The optimized values of the LSSVM⁷² algorithm have been calculated as follows: $\gamma = 1000018$ and $\sigma^2 = 2.87$. The numbers of the reported digits of the two aforementioned parameters are normally obtained by sensitivity analysis of the overall errors of the optimization procedure.

As mentioned earlier, we have already developed two molecular-based models for the same purpose.⁴² The new developed model is more accurate than the previous QSPR-MLR (multivariate linear regression) and QSPR-LSSVM models over representation and prediction of the data in two same data sets.⁴² Moreover, it has been developed more simply and quickly. It should be noted that the current method applies functional

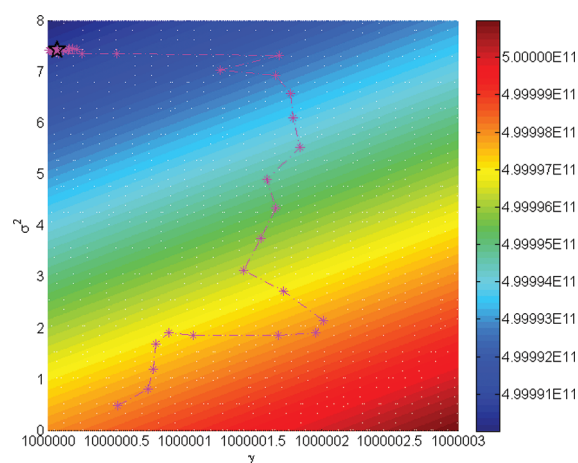


Figure 5. Contour route of the H-GA^{77–79} optimization algorithm in LSSVM⁷² mathematical approach: *, the computational route to converge to the probable global optimum of the problem; ☆, the probable global optimum of the problem. σ^2 and γ are the parameters of the optimization algorithm.

groups that are more familiar than the molecular descriptors of QSPR approach for the engineers working in the industry. The total numbers of the model parameters for both GC-LSSVM and QSPR-LSSVM⁴² are the same (13 parameters). Besides, only few functional groups are present simultaneously in a specified promoter. Therefore, the developed model has few parameters for each compound.

Another factor that merits careful investigation is that we have tried to use almost all of corresponding experimental data^{50–66} available in open literature. However, several error sources in experimental measurements including calibration of pressure transducers, temperature probes, and detectors of gas chromatographs, and possible errors during the measurements of phase equilibria especially those dealing with improper design of the equipment, insufficient experimental time to pass the metastable region, etc.^{87,88} may lead to unreliable experimental data and consequently contribute to decrease the accuracy and prediction capability of the developed models. This would literally demonstrate the need of designing more accurate experimental apparatus and produce reliable experimental data to provide the industry with more accurate and predictive models.^{87–89}

4. CONCLUSION

A novel group contribution model was presented for determination of phase equilibrium of the systems containing structure H clathrate hydrate of water “insoluble” hydrocarbon promoter + methane + water. Almost all of the reported experimental data^{50–66} available in open literature were used for developing and testing the model. The least-squares support vector machine⁷² mathematical tool was combined with group contributions to propose an accurate model. Furthermore, the pattern search hybrid genetic algorithm^{77–79} optimization method has been implemented to optimize the obtained LSSVM⁷² model parameters. The statistical parameters of the final presented model (AAD from experimental values^{50–66} = 1.6%) shows that it is reliable, comprehensive, and predictive method to represent and predict the hydrate dissociation conditions of the systems including sH clathrate hydrates of methane + “insoluble” hydrocarbon promoter + water, which are especially applied in gas

Table A1

GCs	value
T/K	275.2
H01	3
H02	1
H03	1
H04	0
H05	0
H06	0
H07	0
H08	0
H09	0
H10	0
H11	12
H12	4
H13	0

storage processes. Another issue to point out is the effect of uncertainties of the experimental data, applied for developing the model, on the predicted results that cannot be ignored. More accuracy in the experimental measurements of the data, the more accuracy of the developed model would be expected.

APPENDIX. INSTRUCTION FOR USING THE MODEL

To use the developed model, we have organized a computer program. The LSSVM toolbox for MATLAB software should be initially installed. First, one should insert the directory of the toolbox as the main directory in MATLAB environment. Later, it is required to drag and drop the model .mat file into the MATLAB workspace.

Example: Calculation of the clathrate hydrate dissociation pressure of isopentane at 275.2 K. Enter the functional groups (group contributions) for isopentane at 275.2 (see the Supporting Information DOC file). The set of the corresponding functional groups are shown in Table A1

The hydrate dissociation pressure is then calculated simply using the below command line in the workspace:

```
GC=[275.2 3 1 1 0 0 0 0 0 0 12 4 0];
P_calc=simlssvm({'trainV.P','trainV.T',type,gam,
sig2,'RBF_kernel','preprocess'},
{alpha,b},GC)
```

The output result of the program (based on the developed model) will be 2.636 MPa while the corresponding experimental value is 2.650 MPa.

ASSOCIATED CONTENT

S Supporting Information. Detailed information about the investigated heavy hydrocarbon hydrate formers, the group contributions (functional groups), the results of the developed model, and a brief description of the SVM technique are presented in one DOC formats. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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