J. Chem. Lett. 1 (2020) 143-148

Research Article

Journal of Chemistry Letters
journal homepage: www.jchemlett.com
ISSN (online): 2717-1892

Thermodynamic Modeling and Phase Prediction for Binary System Dinitrogen Monoxide and Propane

Behrouz Raei *, Alireza Bozorgian

Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

ARTICLE INFO

Article history:
Received 29 December 2020
Received in revised form 19 February 2021
Accepted 24 February 2021
Available online 25 February 2021

Keywords:
Modeling,
Phase,
Thermodynamic,
Dinitrogen monoxide

ABSTRACT

One of the important activities in chemical engineering is designing and simulating different processes in order to optimize the unit economically and operationally. Thermodynamic and transmissivity properties of fluid in this process are required to be available carefully. In this article, thermodynamic equations operation in PR, SRK, LKP, UNIQUAC in expecting thermodynamic properties and phase operation of binary system of Dinitrogen monoxide and Propane have been studied in order to select the best equations of state (EOS) for simulation. According to the results it is obvious that equation of state PR in expecting Bubble point (P) have mean absolute error equals to 4.98 and mean absolute error in specifying the value of mole fraction of Dinitrogen monoxide in steam phase (Y_1) equals to 0.002338 . It is the minimum error among other models. As a result, alternatively PR, UNIQUAC equations are the best and the weakest models for expecting phase operation and simulating binary system of Dinitrogen monoxide and propane (among considered equations).

1. Introduction

In recent years, the modeling and simulation of physical, chemical and biological processes has received much attention due to its economic importance[1]. As a result, these operations will save a lot of money. But for successful modeling and simulation, the first basic step is adopting appropriate methods for calculating thermodynamic properties[2]. So that the mismatch of the thermodynamic properties calculated with the experimental data can cause modeling inaccuracy or reduce the accuracy of the results of simulation. Therefore, care must be taken in selecting methods and assumptions for predicting physical and thermodynamic properties in modeling and simulation operations. Due to the widespread use of vapor-liquid equilibrium data in various chemical industries, they have been widely studied. In general, the phase behavior of dihydrogen monoxide has been less studied. Physcher *et al.*, [3] conducted the studies under critical conditions for this system and for the nitrogen dioxide and ethane monoxide systems and compared these critical data with the Predictive Soave-Redlich-Kwong equation. In this paper, thermodynamic modeling and prediction of phase behavior of D-nitrogen and propane monoxide systems are performed using four thermodynamic models of Peng - Robinson, Soave - Redlich - Kwong, Lee – Kesler plocker and UNIQUAC. Experimental data equilibrium of vapor equilibrium data from Wagner *et al.*, [4] data were obtained at 10 degrees centigrade.

2. Thermodynamic Model

The polynomial equations, in which the molar volume is of the third degree, have a good relationship between simplicity and generalization, which is suitable for many purposes. In fact, third-degree equations are the simplest equations that can express liquid and vapor behavior [5-8]. Among the third-order mode equations, the Redlich Kwong mode equation will have three strands for volume, between which the two answers may be complex. Relation 1 shows the standard form of the RK mode equation. This equation provides very convincing

* Corresponding author. Tel.: +989113209502; e-mail: b.raei@mhriau.ac.ir

results for calculating vapor-liquid equations. The two SRK and PR equations are derived from the RK mode equation, and have been developed specifically to perform vapor-liquid equilibrium calculations.

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)} \quad (1)$$

a and b are the stability of the equation that depend on the critical properties of the system components [9-14].

3. PR equation

This equation is one of the most widely used models in simulating chemical processes, especially oil, gas and petrochemicals which is used to perform calculations of vapor-liquid equilibrium and the density of hydrocarbon materials. Numerous studies on the primary PR model have shown that the current model can be used for a relatively wide range of single, two and three-phase systems. This equation has several features, including the following [6]:

1. It expresses the parameters based on the critical properties and the decentralization coefficient.
2. It can be used for all calculations, including fluid properties in natural gas processes.
3. For the law of mixing, no more than one parameter of binary interaction should be used and it should be independent of temperature, pressure and composition.
4. The performance results of the model in the vicinity of critical points, especially the calculation of ZC and fluid density must be corrected.

Relation 2 shows the PR equation. (Details of this model are given in Table 1).

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (2)$$

3.1. SRK equation

In many cases, the results of this equation can be compared with the results of the PR equation but often the range proposed for using this equation is more limited [6]. Relation 3 shows the general form of this equation.

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (3)$$

The general equation, theory and scope of application of UNIQUAC and LKP models are described in references [6, 7].

Numerical solution method

In the bubble point pressure calculations of mixture, the following relations is established:

$$\boldsymbol{n_V} = \mathbf{O} \quad \& \quad n_L = 1 \quad \& \quad X_i = Z_i$$
$$1 \le i \le n \quad \sum Z_i K_i = 1 \quad (4)$$

$$\sum Z_i \frac{\phi_i^L}{\phi_i^V} - 1 = 0 \equiv f(P_b) \quad (5)$$

To solve the equation (5), the Newton-Raffson method [15-21] should be used as a guess and deviation.

$$\sum \frac{Z_i \phi_i^V \left(\frac{\partial \phi_i^L}{\partial P}\right)}{\left(\phi_i^V\right)^2} - \sum \frac{Z_i \phi_i^L \left(\frac{\partial \phi_i^V}{\partial P}\right)}{\left(\phi_i^V\right)^2} \equiv f'(P_b) \quad (6)$$

$$P^{(K+1)} = P^{(K)} - \frac{f(P_b)}{f'(P_b)} \quad (7)$$

3.2. Thermodynamic modeling of vapor-liquid equilibrium

In this paper, the aim of thermodynamic modeling was to predict the phase behavior of the di-nitrogen monoxide (1) and propane (2) binary systems using 4 models: PR, SRK, LKP and UNIQUAC. The procedure is as follows: In each relative compound, the di-nitrogen monoxide component in the liquid phase (X_1), the bubble point (P) and its relative composition in the vapor phase (Y_1) are obtained using the mentioned models and then compared with the data. Empirically, the difference for each data from Equation 8 was calculated. The average absolute deviation rate was then calculated using Equation 9 and the maximum deviation value for each thermodynamic model. Finally, the model with the lowest absolute average deviation rate was selected as the most appropriate thermodynamic model for system design and simulation calculations. It should be noted that the simulation of experimental data and all calculations was done with the help of software[22-28].

Diff (Error) = Experimental value - Computational value (8)

$$\text{Mean absolute error} = \sum \frac{|Diff|}{n} \quad (9)$$

Table 1 shows the phase equilibrium laboratory data (P-xy) of the di-nitrogen monoxide (1) and propane (2) systems obtained by Wagner *et al.* [4] at 10 degrees centigrade.

Table 1. Experimental data of di-nitrogen and propane monoxide system [4]

P (kPa)	X_1	Y_1
638.5	0	0
906.1	0.0699	0.3068
1208.4	0.155	0.4978
1386	0.2016	0.5649
1621	0.2687	0.6383
1864.6	0.3401	0.6964
2312.3	0.4751	0.7774
2458.2	0.5136	0.7972
2671.2	0.585	0.8269
2709.7	0.5954	0.8312
3003.1	0.689	0.8687
3082.8	0.7082	0.8767
3405.3	0.8153	0.9179
3637.1	0.883	0.9466
3864.7	0.9502	0.9761
3996.9	0.9869	0.9934
4041.3	1	1

4. Results

Due to the length of the calculations, it is enough to mention the results obtained for the PR model in the form of Table 2.

Table 2. Results from modeling with PR equation of state

Mole fraction of dihydrogen monoxide in the liquid phase (X_1)	Error in bubble point calculation (Diff P)	Error in calculating the mole fraction of di nitrogen monoxide in the vapor phase (Diff Y)
0	2.19	0
0.0699	-4.29	-0.009
0.155	5.04	-0.0057
0.2016	-5.03	-0.0038
0.2687	-2.84	-0.0014
0.3401	0.67	0.001
0.4751	6.07	0.0023
0.5136	-13.59	0.00078
0.585	4.72	0.0031
0.5954	-0.29	0.0035
0.689	6.44	0.0025
0.7082	-11.73	0.0015
0.8153	12.16	0.00126
0.883	4.07	0.00056
0.9502	4.27	-0.00069
0.9869	-0.78	-0.00017
1	0.47	0
Mean absolute error	4.98	0.002338
Maximum error	13.59	0.009

In Table 3, the mean absolute error values of the different models are compared.

Table 3. The Mean absolute error of different models

Model	Bubble point (P)	Mole fraction of di-nitrogen monoxide in the vapor phase (Y_1)
PR	4.98	0.002338
SRK	121.31	0.00709
LKP	45.69	0.00354
UNIQUAC	111.43	0.0573

According to the results obtained from Table 3, it can be seen that the thermodynamic PR model due to having the lowest mean absolute error in predicting the bubble point (P) which is equal to 4.98 and except for the molar equilibrium of di-nitrogen monoxide in the vapor phase (Y_1) which is equal to 0.002338, the most suitable thermodynamic model for predicting vapor equilibrium behavior is the fluid of this system. Figures 1, 2, 3 and 4 graphically compare the experimental data (P-xy) with the results obtained from different thermodynamic models.

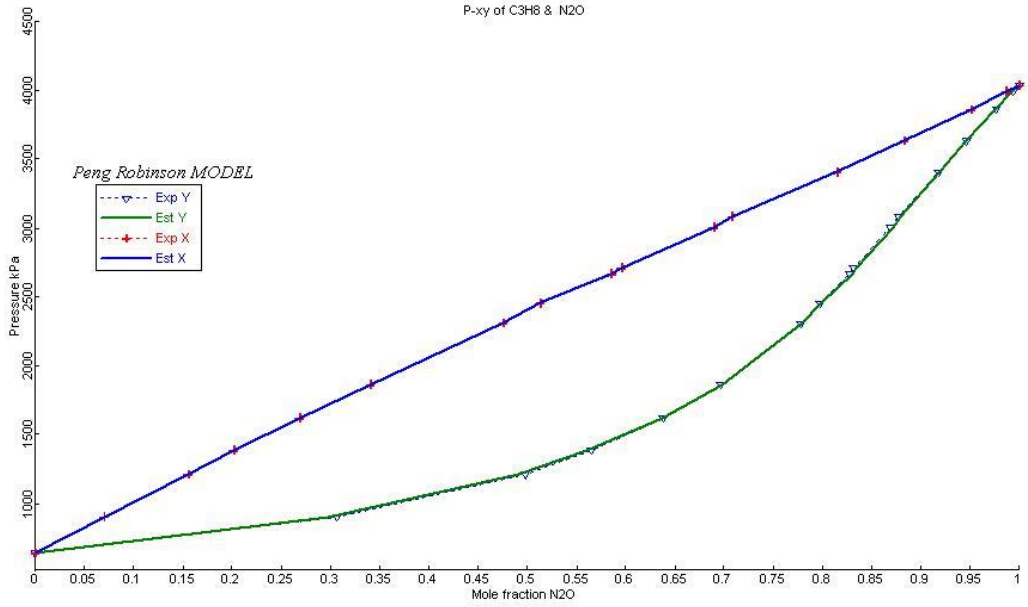

Figure 1. Comparison of experimental data with the results obtained from the PR

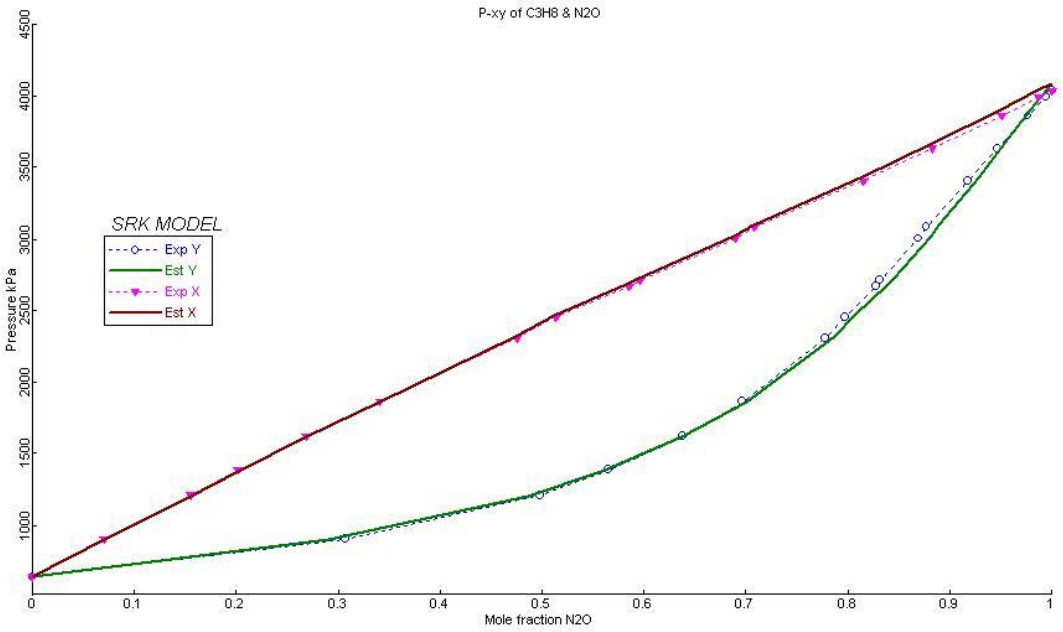

Figure 2. Comparison of experimental data with the results obtained from the SRK

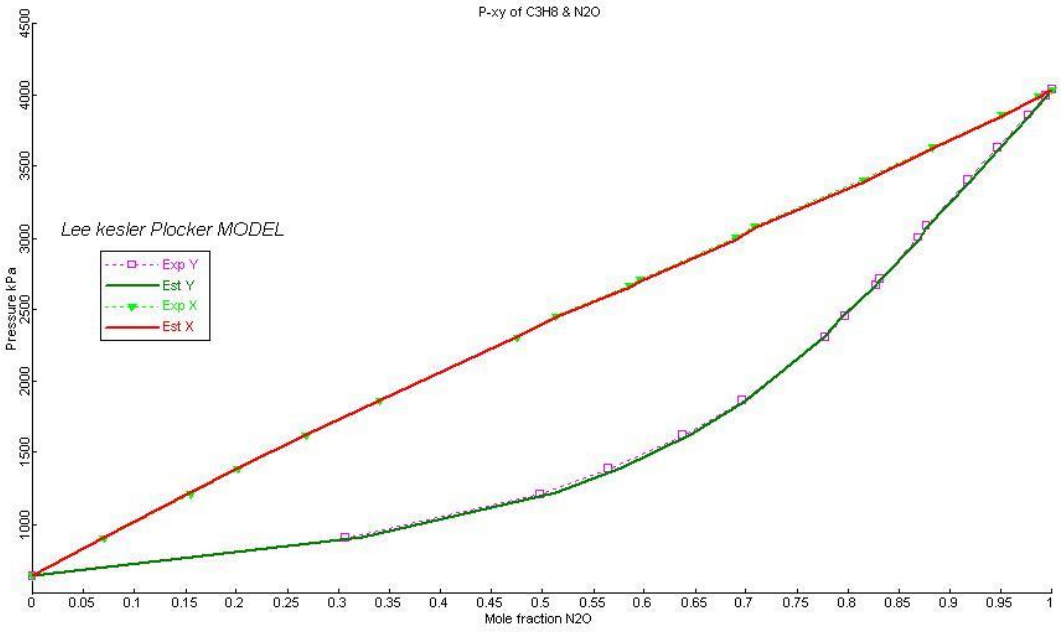

Figure 3. Comparison of experimental data with the results obtained from the LKP

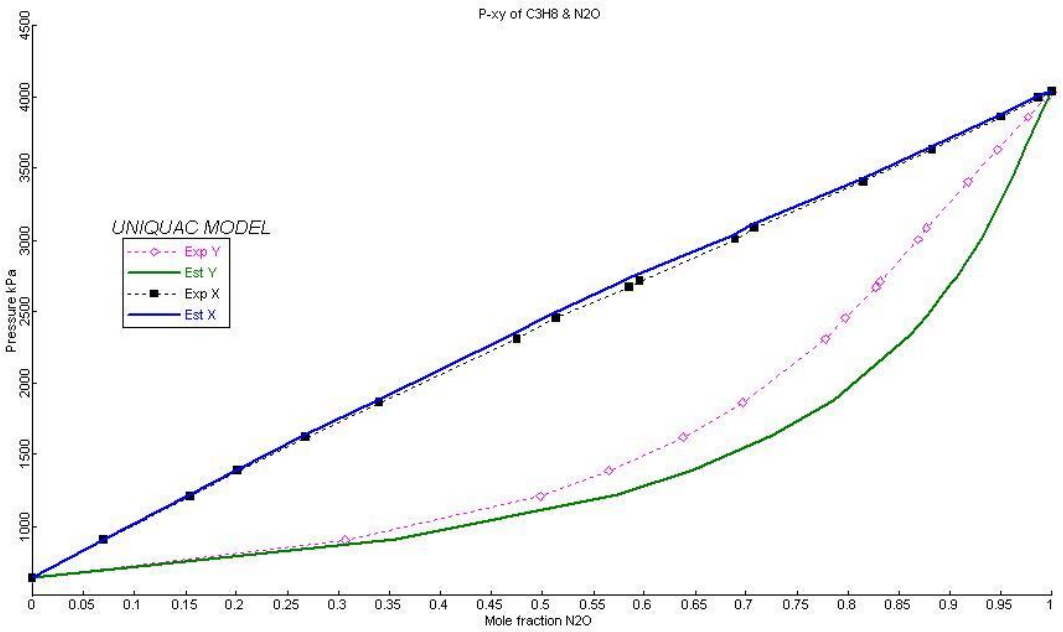

Figure 4. Comparison of experimental data with the results obtained from the UNIQUAC

A graphical comparison between experimental data and the computational results obtained from different models confirms the results of Table 4. As shown in the diagrams, the thermodynamic PR model (Figure 1) is better able to cover experimental data than other models (with the least deviation). However, the use of the UNIQUAC model for predicting the liquid phase and considering the ideal mode for the gas phase (Figure 4) has the greatest deviation and non-compliance of experimental data with computational data and is the weakest model among the studied models for predicting phase behavior of di-nitrogen monoxide and propane system.

5. Conclusion

In this study, the phase behavior of the di-nitrogen monoxide and propane systems has been modeled by 4 thermodynamic models PR, SRK, LKP and UNIQUAC. Calculating the mean absolute error in predicting the bubble point (P) and molar fraction other than the di-nitrogen monoxide in the vapor phase (Y_1) shows that the PR equation has the lowest mean absolute error, therefore, the best model for predicting the phase behavior of this system (among the models studied). Also, using the UNIQUAC model to predict the liquid phase and considering the ideal mode for predicting the gas phase can in no way accurately predict the system's equilibrium behavior and it has the highest mean absolute error among the models. In addition, the graphical comparison of the computational results by modeling with the experimental equilibrium data (P-xy) of Wagner *et al.* confirms these results. In general, differences in computational results with experimental data in predicting the phase behavior of a system can be combined due to the complex nature of the molecules and the mixing relations used to determine the molecular interaction.

References

[1] J.C. Lima, et al., Phase behavior data and thermodynamic modeling of the binary system {CO2+ COUMARIN} at high pressures. *Braz. J. Chem. Eng*., 36 (2019) 1053-1059.

[2] A. Bozorgian and M. Ghazinezhad, A Case Study on Causes of Scale Formation-Induced Damage in Boiler Tubes. *J. Biochem. Tech.*, 2 (2018) 139-153.

[3] N. Juntarachat, et al., Validation of a new apparatus using the dynamic method for determining the critical properties of binary gas/gas mixtures. *J. Chem. Eng. Data*, 58 (2013) 671-676.

[4] J. Mashhadizadeh, A. Bozorgian, A. Azimi, Investigation of the kinetics of formation of Clatrit-like dual hydrates TBAC in the presence of CTAB. *Eurasian Chem. Commun.*, 2 (2020) 536-547.

[5] A. Bozorgian, Study of the Effect Operational Parameters on the super critical Extraction Efficient Related to Sunflower Oil Seeds. *Chem. Rev. Lett.*, 3 (2020) 94-97.

[6] M. Esmaeili Bidhendi, Z. Asadi, A. Bozorgian, A. Shahhoseini, M.A. Gabris, S. Shahabuddin, R. Khanam, R. Saidur, New magnetic Co3O4/Fe3O4 doped polyaniline nanocomposite for the effective and rapid removal of nitrate ions from ground *water samples. Environmental Progress & Sustainable Energy*, p.e13306 (2019).

[7] A. Bozorgian, Investigation and comparison of experimental data of ethylene dichloride adsorption by Bagasse with adsorption isotherm models. *Chem. Rev. Lett.*, 3 (2020) 79-85.

[8] E. Mousavi, A. Bozorgian, Investigation the Kinetics of CO2 Hydrate Formation in the Water System + CTAB + TBAF + ZnO. *Int. J. New Chem.*, 7 (2020), 195-219

[9] A. Bozorgian, A. Samimi, review of Kinetics of Hydrate Formation and the Mechanism of the Effect of the inhibitors on it. *Int. J. New Chem*., 8 (2020), 41-58

[10] A. Bozorgian, The Production of Clay Nano-Composite Epoxy and Comparison of Its Properties with Epoxy Resins. *Polymer*, 2 (2012) 12923-12929.

[11] A.H. Tarighaleslami, A. Bozorgian, B. Raei, Application of the energy analysis in the petroleum refining processes optimization. *In The 1st Territorial Chemistry and Industry*

Symposium, Lecture number: E-1097, Damghan, Iran (in Persian), (2009).
[12] A. Bozorgian, Z.A. Aboosadi, A. Mohammadi, B. Honarvar, A. Azimi, Evaluation of the effect of nonionic surfactants and TBAC on surface tension of CO2 gas hydrate. *J. Chem. Pet. Eng.*, 54 (2020), 73-81.
[13] A. Bozorgian, Analysis and simulating recuperator impact on the thermodynamic performance of the combined water-ammonia cycle, *Prog. Chem. Biochem. Res.* 3 (2020), 169-179.
[14] A. Bozorgian, Methods of Predicting Hydrates Formation, *Adv. J. Sci. Eng.*, 1 (2020), 34-39.
[15] A. Bozorgian, Investigation of Predictive Methods of Gas Hydrate Formation in Natural Gas Transmission Pipelines, *Adv. J. Chem. B*, 2 (2020), 91-101.
[16] A. Bozorgian, Investigation of the history of formation of gas hydrates, *J. Eng. Indu. Res.* 1 (2020), 1-19.
[17] A Bozorgian, Investigation of Hydrate Formation Phenomenon and Hydrate Inhibitors, *J. Eng. Indu. Res.* 1 (2020), 99-110.
[18] Siadati, S. A., & Mirabi, A. Diels-Alder versus 1, 3-dipolar cycloaddition pathways in the reaction of C20 fullerene and 2-furan nitrile oxide. Progress in Reaction Kinetics and Mechanism, 40(4), (2015)383-390.
[19] Zardoost, M. R., & Siadati, S. A. A DFT study on the cycloaddition of dimethyl acetylenedicarboxylate and 3, 4-dihydroisoquinoline-N-oxide. Progress in Reaction Kinetics and Mechanism, 37(4), (2012)436-441.
[20] Zardoost, M. R., & Siadati, S. A. A DFT study on the effect of functional groups on the formation of 1, 2, 3-triazolo-1, 4-benzoxazine intramolecular 1, 3-dipolar cycloaddition. Progress in Reaction Kinetics and Mechanism, 38(2), (2013)191-196.
[21] Zardoost, M. R., Siadati, S. A., & Oghani, B. G. A DFT study on the 1, 3-dipolar Mechanism, 38(3), (2013) 316-322.
[22] A. Bozorgian, Investigation of Predictive Methods of Gas Hydrate Formation in Natural Gas Transmission Pipelines, *Adv. J. Chem. B*, 2(3) (2020), 91-101.
[23] A. Bozorgian, Methods of Predicting Hydrates Formation, *Adv. J. Sci. Eng.*1 (2) (2020), 34-39.
[24] A. Bozorgian, N. Majdi Nasab, and H. Mirzazadeh, Overall effect of nano clay on the physical mechanical properties of epoxy resin. *World Academy of Science, Engineering and Technology International Journal of Materials and Metallurgical Engineering 5*, no. 1 (2011) 21-24.
[25] A. Bozorgian, Z. Arab Aboosadi, A. Mohammadi, B. Honarvar, and A. Azimi. Optimization of determination of CO2 gas hydrates surface tension in the presence of non-ionic surfactants and TBAC. *Eurasian Chemical Communications*, 2 (2020) 420-426.
[26] B. Raei, A. Ghadi, and A. R. Bozorgian. Heat Integration of heat exchangers network using pinch technology. In 19th International Congress of Chemical and Process Engineering CHISA. 2010.
[27] A. Bozorgian, Z. Arab Aboosadi, A. Mohammadi, B. Honarvar, and A. Azimi, Prediction of Gas Hydrate Formation in Industries. *Progress in Chemical and Biochemical Research*, 3 (2020) 31-38.
[28] S.V. Mousavi, A. Bozorgian, N. Mokhtari, M.A. Gabris, H. Rashidi Nodeh, and W. Aini Wan Ibrahim. A novel cyanopropylsilane-functionalized titanium oxide magnetic nanoparticle for the adsorption of nickel and lead ions from industrial wastewater: Equilibrium, kinetic and thermodynamic studies. *Microchemical Journal*, 145 (2019) 914-920.