

Study on Redressing the Thermodynamic Property Package for Process Simulator

Vikas Dinkar Gosavi ^{1*}, Mohini Premmurari Dubey ¹

¹Department of Chemical Engineering, Institute of Technology, Nirma University, Ahmedabad 382481, Gujarat, India

Abstract

This paper describes the importance of redression of binary interaction parameter for selected thermodynamic property package in process simulator. The work has been made in this paper to redress the binary interaction parameter for non-ideal or complex binary systems of 2-ethoxyethanol + di-n-propyl ether, 1-propanol + 2-ethoxyethanol, 1-propanol + di-n-propyl ether. In this study, redressed value of the binary interaction parameters for UNIQUAC model fitted in CHEMCAD simulation software for comparing the bubble point pressure from experimental data and simulator data to increase the accuracy of simulation result.

Keywords: Activity coefficient, Binary interaction parameter, Redression, Regression, 2-ethoxyethanol, 1-propanol.

1. Introduction

Di-n-propyl ether (DPE) can be manufactured from reaction of 1-propanol (PA) with H₂SO₄, and complete separation of di-n-propyl ether can be archived with the help of 2-ethoxyethanol (trade name is Cellosolve) as solvent. Cellosolve mainly used as a solvent in industries or laboratory practices to dissolve resin, waxes, lacquers, grease, oils and nitrocellulose. Extractive distillation operation is used for separation of a DPE + PA. Cellosolve form a complex or non-ideal mixture with 1-propanol and di-n-propyl ether [1]. For designing of a distillation system vapor liquid equilibrium (VLE) data play vital role in it [2]. Process simulator like CHEMCAD simulation software can be used for design of such distillation system.

Process simulator is an outstanding tool for analyzing, designing, rating and optimizing the process plants, refineries, chemical plants. In process simulator, various kind of thermodynamic property packages are used such as equation of state (EOS), activity models, vapor pressure models, chao seader and grayson streed

models, other special models etc. Mainly thermodynamic activity models are used for non-standard or complex system. Binary interaction parameter (BIP) is the heart of the activity model and its value calculated with the help of the data regression analysis from experimental vapor liquid equilibrium (VLE) data. However, no one of activity model is accurate and often some adjustment must be done before their applications. Researchers have already provided BIP data for various mixtures in databank of process simulator. Before actual simulation, must check the accuracy and validity of thermodynamic property package. Convergence of flowsheet in process simulator does not give the guaranty of correct results [3]. Use of improper redressed binary interaction parameter (BIP) in process simulator which generates the result which deviates from reality. Prior to their application of process simulator with thermodynamic property package redressing of the binary interaction parameter with checking the converged result and its accuracy within allowable range, if not then thermodynamic property package should be redressed to enhance its accuracy [4]. This redressing can be done by VLE calculation such as dew point, bubble point or flash calculation and comparing the result with experimental data. Experimental VLE data for 2-ethoxyethanol + DPE (Table 1) [5], PA + 2-ethoxyethanol (Table 2) [6], PA + DPE (Table 3) [7] system has taken from literature and simulated VLE data is generated from CHEMCAD V6.0, using UNIQUAC thermodynamic activity model.

2. Theory

2.1. UNIQUAC Activity Model

UNIQUAC equation is equipped with two parts; a combinatorial part of UNIQUAC equation is describing the entropic contribution and residual part stand for the intermolecular forces. The combinatorial part requires only pure component data like sizes and shapes of molecules. The two binary interaction parameters arise only in the residual part of UNIQUAC equation [8].

The UNIQUAC equation, substituting $\frac{G^E}{RT} = G$, is given by

$$G = G^C(\text{combinatorial}) + G^R(\text{residual}) \quad (1)$$

$$G^C = \left[x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + z \left(q_1 x_1 \ln \frac{\phi_1}{\phi_1} + q_2 x_2 \ln \frac{\phi_2}{\phi_2} \right) \right]$$

$$G^R = [-q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12})]$$

Where,

$$\Theta_i = \text{Area fraction of component } i = \frac{x_i q_i}{\sum x_j q_j}$$

$$\Phi_i = \text{Volume fraction of component } i = \frac{x_i r_i}{\sum x_j r_j}$$

q_i = Surface area parameter of component i

r_i = Volume parameter of component i

τ_{ij} = Area Parameter

$$= \exp \left[A_{ij} - \frac{(U_{ij} - U_{ji})}{RT} + C_{ij} \ln(T) + D_{ij} T \right]$$

T = Temperature in degrees Kelvin

Z = 10 (coordination number)

The UNIQUAC BIP's of A_{ij} , $(U_{ij} - U_{ji})$, and $(U_{ji} - U_{ii})$ are in cal/gmol. The binary interaction parameters C_{ij} and D_{ij} are optional. When regressing BIP's for UNIQUAC model, calculates only $(U_{ij} - U_{ji})$, and $(U_{ji} - U_{ii})$ with considering A_{ij} and A_{ji} are set to zero.

2.2 Effect of BIP on prediction of bubble point pressure

Bubble point pressure is defined as the pressure point at which the first bubble of gas comes out of the solution. At constant temperature bubble point pressure data with their corresponding liquid composition data arise from VLE experiment. According to the research studies, BIP value shows inherent temperature dependency [9,10]. The degree of temperature dependency of BIP is closely related to complexity in thermodynamic model. Those complexities increase the temperature dependency of BIP which lead to decrease the property prediction ability [11]. BIP is an empirical value and it has no theoretical explanation. Binary interaction parameters are calculated from data regression analysis. In data regression analysis, minimise the objective function to find out the accurate binary interaction parameter for thermodynamic model [12,13]. UNIQUAC model were capable of precisely correlating the highly non-ideal or complex binary and ternary systems [14]. For redressing the BIP, try to simulate the same condition with UNIQUAC model in CHEMCAD simulator as the condition at which experimental data were obtained, and observed how accurately the model can match them. Then find out the absolute relative deviation (ARD) from simulated result and experimental value.

$$\% \text{ ARD} = \frac{1}{N} \sum_i^N \left| \frac{P_{\text{exp}} - P_{\text{sim}}}{P_{\text{exp}}} \right| \times 100$$

Table 1: Experimental vapor-liquid equilibrium data for the binary system of 2-ethoxyethanol (1) + di-n-propyl ether (2) at 333.15K [5]

P (N/m ²)	X ₁
37092	0.0000
36634	0.0395
35738	0.0895
34283	0.1778
32637	0.2878
30856	0.4081
28594	0.5361
26455	0.6310
23462	0.7311
21037	0.7923
17717	0.8573
14328	0.9072
11746	0.9414
9057	0.9655
7471	0.9817
6787	0.9864
5874	0.9947
5486	0.9981
5278	1.0000

Table 2: Experimental vapor-liquid equilibrium data for the binary system of n-propyl alcohol (1) + 2-ethoxyethanol (2) at 313.15K [6]

P (N/m ²)	X ₁
1865	0.0000
2046	0.0298
2224	0.0606
2452	0.1001
2732	0.1500
3005	0.1997
3282	0.2503
3550	0.2997
3813	0.3497
4070	0.3997
4326	0.4498
4578	0.4998
4825	0.5498
4829	0.5499
5072	0.5999
5309	0.6499
5554	0.7000
5785	0.7498
6022	0.7998
6249	0.8496
6477	0.8998
6662	0.9401
6785	0.9701
6939	1.0000

Step to analyze the effect of BIP on prediction of bubble point pressure:-

- 1) Find out the BIP's $(U_{ij} - U_{ii})$ and $(U_{ji} - U_{jj})$ for UNIQUAC model from data regression with help of experimental VLE data.

- 2) Compared the experimental values with result generated from process simulator with default value of BIP's as well as redressed value of BIP's.
- 3) Calculate the average relative deviation (ARD) between experimental values and CHEMCAD simulator generated result.
- 4) Redresses the BIP to minimize the %ARD till simulated result match with experimental value.

Table 3: Experimental vapor-liquid equilibrium data for the binary system of n-propyl alcohol (1) + di-n-propyl ether (2) at 333.15K [7]

P (N/m ²)	X ₁
25145	0.0000
26566	0.0842
26772	0.1105
26923	0.1462
27019	0.1759
27116	0.2037
27026	0.2854
26379	0.4165
25521	0.5314
25093	0.5821
23070	0.7128
22891	0.7226
20953	0.8075
16117	0.9337
12238	1.0000

3. Result and Discussion

The effects of BIP ($U_{ij}-U_{ii} / U_{ji}-U_{jj}$) on bubble point pressure for mixture 2-ethoxyethanol (i) + DPE (j) at 333.15K for a 2-ethoxyethanol in liquid phase were forecasted using UNIQUAC in CHEMCAD V 6.0. Initially, the default value of the BIP in the databank of CHEMCAD $U_{ij}-U_{ii} = 0$ and $U_{ji}-U_{jj} = 0$ was used. The simulator generator result compared with experimental data and average relative deviation (ARD) for nineteen data point to be 20.347%. Redressed value of BIPs $U_{ij}-U_{ii} = -249.89$ and $U_{ji}-U_{jj} = 629.102$ was predicted with the help of data regression analysis of experimental value with UNIQUAC model. That redressed value of BIPs was reducing the 20.347% ARD to 3.483% ARD. The effects of BIP on bubble point pressure graphically represented in fig 1. That figure 1 clearly shows that the importance of redression of BIP for improving the accuracy of simulation result. Redression is substantial and accuracy of simulation much more improved. Similar improvements are observed for binary mixtures of PA (i) + 2-ethoxyethanol (j) and PA (i) + DPE (j) at 313.15K and 323.15K respectively, the default value of BIP in databank of CHEMCAD for both binary mixtures are $U_{ij}-U_{ii} = 0$ and $U_{ji}-U_{jj} = 0$ and redressed value of BIP for binary mixtures of PA (i) + 2-ethoxyethanol (j) and PA (i) + DPE (j) are tabulated in

table 4. Compare the simulator generated results of bubble point pressure for binary mixtures of PA (i) + 2-ethoxyethanol (j) and PA (i) + DPE (j) with their corresponding experimental data and that comparison graphically demonstrates in figure 2 and 3 respectively. Reductions in average relative deviation (ARD) for binary mixtures of PA (i) + 2-ethoxyethanol (j) and PA (i) + DPE (j) are tabulated in table 5.

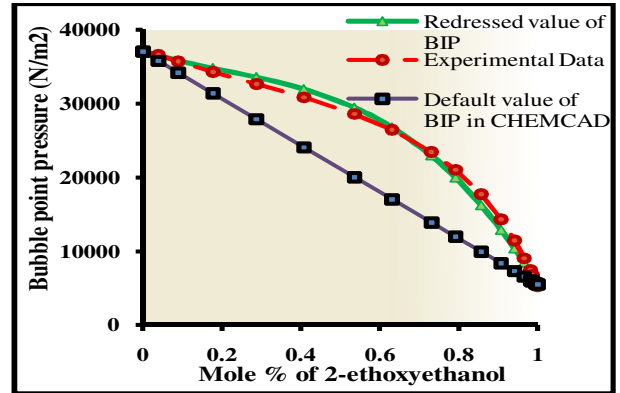


Figure 1: Effect of BIP on B.P.P. of 2-ethoxyethanol + DPE at 333.15K

Table 4: BIP for binary mixture

Binary mixture	Default value of BIP in CHEMCAD	Redressed value of BIP
2-ethoxyethanol (i) + DPE (j)	$U_{ij}-U_{ii} = 0$ $U_{ji}-U_{jj} = 0$	$U_{ij}-U_{ii} = -249.89$ $U_{ji}-U_{jj} = 629.102$
PA (i) + 2-ethoxyethanol (j)	$U_{ij}-U_{ii} = 0$ $U_{ji}-U_{jj} = 0$	$U_{ij}-U_{ii} = -69.3672$ $U_{ji}-U_{jj} = 116.633$
PA (i) + DPE (j)	$U_{ij}-U_{ii} = 0$ $U_{ji}-U_{jj} = 0$	$U_{ij}-U_{ii} = -240.7538$ $U_{ji}-U_{jj} = 703.182$

Redressed values of BIP in UNIQUAC model has been shown remarkable improvement in the simulation result. Table 5 clearly shows that the importance of binary interaction parameters in UNIQUAC for enhancing the predictability of process simulator. Remarkable improvement is observed in % ARD for binary systems of 2-ethoxyethanol + DPE, PA + 2-ethoxyethanol, PA + DPE. Property prediction of the binary and ternary systems or behaviour of the system with other process variable is greatly predicted with the help of redressed value of BIP in model.

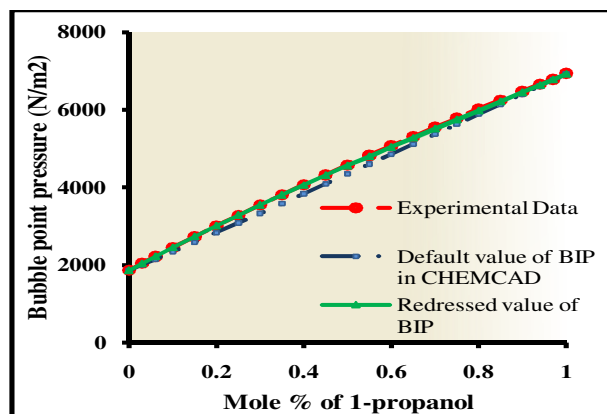


Figure 2: Effect of BIP on B.P.P. of PA + 2-ethoxyethanol at 313.15K

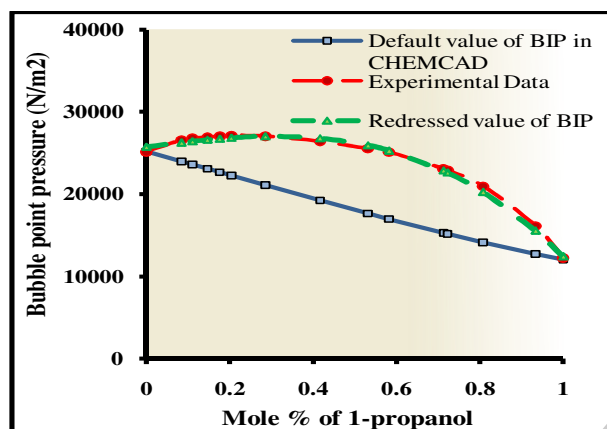


Figure 3: Effect of BIP on B.P.P. of PA + DPE at 323.15K

Table 5: Average relative deviations for binary mixture

Binary mixture	% ARD with default value of BIP	% ARD with redressed value of BIP
2-ethoxyethanol (i) + DPE (j)	20.347 %	3.483 %
PA (i) + 2-ethoxyethanol (j)	3.530 %	0.36398 %
PA (i) + DPE (j)	20.311 %	1.154 %

4. Conclusion

This paper demonstrate that the binary interaction parameters of an UNIQUAC model can be redressed to enhance the accuracy of process simulator considerably and also provide a step wise procedure for redression of the binary interaction parameter for thermodynamic model in process simulator. In this work, current discrepancies between default value of BIP in CHEMCAD simulation software and redressed value of BIP were analysed and study the impact of redression of binary interaction parameter for prediction of bubble point pressure for given system. These studies are clearly shows that the necessities of validation of the accuracy of thermodynamic models prior to performing simulation work. While accurately redressed value of BIP's for thermodynamic model in process simulator which has ensures that the simulator generated result as good as experimental value.

5. Acknowledgements

The authors would like to acknowledge from beneath of the heart to the Department of Chemical Engineering, Nirma University for providing congenial environment for completing this study.

6. References

- [1] E. Lladosa, J.B. Monton, M.C. Burguet, R. Munoz, "Phase equilibria involved in extractive distillation of dipropyl ether + 1-propyl alcohol using 2-ethoxyethanol as entrainer", *Fluid Phase Equilibria* 255 (2007) pp. 62-69.
- [2] O.T. Olaleke, F.O. Chukwuma, B.O. Evuomwan, "Vapor-liquid equilibrium calculation of multi-components system with estimation of pre-heat temperature", *British Journal of Applied Science and Technology* 3 (2013) pp. 1-16.
- [3] F. H. Case, A. Chaka, J. D. Moore, R. D. Mountain, J. D. Olson, R. B. Ross, M. Schiller, V. K. Shen, E. A. Stahlberg, "The fifth industrial fluid properties simulation challenge", *Fluid Phase Equilibria* 285 (2009) pp. 1-3.
- [4] H. Utami, S. Roto, W. B. Sediawan, "Liquid-liquid equilibrium for the binary mixtures of α -pinene + water and α -terpineol + water", *World Academy of Science, Engineering and Technology* 78 (2013) pp. 851-854.
- [5] M. Antosik, Z. Frasz, S. K. Malanowski, "Vapor-liquid equilibrium in 2-ethoxyethanol + valeraldehyde and + propyl ether at 313.15 to 333.15K", *Journal of Chemical Engineering Data* 47 (2002) pp. 757-760.
- [6] S. Pathare, V. R. Bhethanabotla and S.W. Campbell, "Total vapor pressure measurements for 2-ethoxyethanol with carbon tetrachloride, chloroform, and dichloromethane at 303.15K," *Journal of Chemical Engineering Data* 49 (2004) pp. 510-513.
- [7] R. Garriga, F. Sanchez, P. Perez, M. Gracia, "Isothermal vapor-liquid equilibrium at eight temperatures and excess functions at 298.15K of di-n-propylether with 1-propanol or 2-propanol", *Fluid Phase Equilibria* 138 (1997) pp. 131-14.

- [8] M.B. Mane, and S. N. Shinde, "Vapor liquid equilibria: A review", *Scientific reviews & Chemical communications* 2 (2012) pp. 158-171.
- [9] L.A. Pellegrini, S. Moioli, S. Gamba, P. Ceragioli, "Prediction of vapor-liquid equilibrium for reservoir mixture with cubic equations of state: Binary interaction parameters for acidic", *Fluid Phase Equilibria* 326 (2012) pp. 45-49.
- [10] J-N. Jaubert, F. Mutelet, "VLE predictions with the Peng-Robinson equation of state and temperature dependent kij calculated through a group contribution method", *Fluid Phase Equilibria* 224 (2004) pp. 285-304.
- [11] S.K. Fateen, M.M. Khalil, A.O. Elnabawy, "Semi-empirical correlation for binary interaction parameters of the Peng-Robinson equation of state with the van der waals mixing rules for the prediction of high-pressure vapor-liquid equilibrium", *Journal of Advanced Research* 4 (2013) pp. 137-145.
- [12] I. Ashour, G. Aly, "Effect of computation techniques for equation of state binary interaction parameters on the prediction of binary VLE data", *Computers & Chemical Engineering* 20 (1996) pp. 79-91.
- [13] M.E. Araujo, M.A.A. "Improving phase equilibrium calculation with the Peng-Robinson EOS for fats and oils related compounds/supercritical CO₂ systems", *Fluid Phase Equilibria* 169 (2000) pp. 49-64.
- [14] S. Chovau, B. V. Bruggen, P. Luis, "Application of the mass-based UNIQUAC model to membrane systems: A critical revision", *Journal of Chemical Thermodynamics* 48 (2012) pp. 260-266.

IJERT