Journal of Chemical Engineering and Materials Science Vol. 3(4), pp. 58-64, November, 2012
Available online at http://www.academicjournals.org/JCEMS
DOI: 10.5897/JCEMS11.058
ISSN-2141-6605 JCEMS ©2012 Academic Journals

Full Length Research Paper

Comparison of unconstrained search methods for correlation of binary vapor liquid equilibrium (VLE) by five variants of Wilson model

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Accepted 20 June, 2012

A comparative evaluation of five variants of Wilson model and eight unconstrained optimization methods for correlating the binary VLE data of 2-butanol-Tetrachloroethene system at 101.08 kPa pressure is presented. The data reduction and correlation for vapor/liquid equilibrium of the above system is presented. The objective of this paper was to find the parameters of the five variants of the Wilson models for the 2-butanol-tetrachloroethene, using optimization methods. The application of this optimization method for thermodynamic calculations is versatile due to its reliability, and efficiency is tested using phase equilibrium and parameter estimation problems. The obtained results indicated that proposed methodology is generally robust for the minimization of the objective functions involved in flash calculations using Gibbs energy minimization and in the calculation of homogeneous in non-reactive mixtures.

Key words: Binary VLE, 2-butanol, tetrachloroethene, unconstrained search methods, Wilson model, phase equilibria.

INTRODUCTION

The correlation of binary vapor liquid equilibrium data is very important as it provides parameters in describing the G^E/activity coefficient models which can in turn be used for the design and simulation of distillation equipment, and also for testing theories of liquid mixtures. Most of the liquid mixtures encountered in commercial operations are non ideal. The non ideality in a liquid mixture can be concisely represented by the Excess Gibbs free energy $\left(G^E/RT = g^E\right)$. There are several empirical and semi-theoretical models proposed in literature (Ravi, 2004). The g^E models can be broadly classified as classical models and models based on local composition concept. Often, they are classified as enthalpic (h^E) models, entropic (s^E) models and complete g^E models $\left(g^E = h^E - Ts^E\right)$ (Ravi Prasad, 2004). The latest G^E models offer the advantage that the multi-component VLE data can be predicted using the parameters of the constituent binary pairs, only without any experimental data on the multi-component mixture. The correlation of binary VLE (P-T-x-y) data consists in the determination of the constants in the G^E model by minimizing the objective function $\sum\left(g^E_{exp} - g^E_{cal}\right)^2$. Minimization of other objective functions is also possible. The constants can be obtained by several methods based on either solution of sets of non linear equations or optimization.

In Chemical Engineering, several thermodynamic calculations can be formulated as optimization problems with or without restrictions. As indicated by Henderson et al. (2004), the formulation of thermodynamic calculations

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for optimization problems offers some advantages: (a) the use of a robust optimization method, (b) the possibility of using a direct optimization method which requires only calculations of the objective function and (c) the use of an iterative procedure whose convergence is almost independent of the initial guesses. Some examples of these calculations are phase stability analysis, phase equilibrium problems, parameter estimation in thermodynamic models, calculation of critical points, among others. In this paper, as part of a continuing study of comparative evaluation of G^E/γ models and parameter estimation methods, eight methods of unconstrained optimization, namely Hooke-Jeeves, Powell, Rosenbrock, Nelder-Mead simplex, Cyclic coordinate, Random search, Simulated annealing and Genetic algorithm (Ashok and Tirupati, 1999) are applied to obtain parameters in five variants of Wilson model namely Wilson (1964), Enthalpic Wilson (Bruin, 1976), Effective Wilson (Sabarattinam et al., 1977), Modified Wilson (Huang and Lee, 1996) and T. K. Wilson (Tsuboka and Katayama, 1975) to describe the vapor liquid equilibrium data of 2-butanol-tetrachloroethene at 101.08 kPa (Venkateswara Rao and Ravi Prasad, 1984).

MATERIALS AND METHODS

Procedure for parameter estimation

1. The properties needed for processing and the experimental P, T, x, y data is read.

2. The g^E_{exp} is calculated using $g^E_{exp} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ with $\gamma_i = y_i P / x_i P_i^{sat}$. The vapor phase is assumed to be ideal.

3. The g^E_{cal} values are calculated using the selected model equation and using the assumed set of parameters.

4. The expression $\left(g^E_{exp} - g^E_{cal}\right)^2$ is minimized using the selected optimization method.

5. With the optimized parameters vapor composition is calculated and absolute average deviation in experimental vapor composition and calculated vapor composition is evaluated

Variants of Wilson G^E models

The five variants of Wilson G^E models used in this study are listed below.

Wilson (1964)

$$\Lambda_{12} = \frac{V_2}{V_1}\mathrm{EXP}\left(-\frac{A_{12}}{RT}\right); \qquad \Lambda_{21} = \frac{V_1}{V_2}\mathrm{EXP}\left(-\frac{A_{21}}{RT}\right); \quad \text{and}$$

$$\left(\frac{G^E}{RT}\right)_{CAL} = -X_1 \ln\left(X_1 + \Lambda_{12}X_2\right) - X_2 \ln\left(X_2 + \Lambda_{21}X_1\right)$$

Enthalpic Wilson (Bruin, 1976)

$$\left(\frac{G^E}{RT}\right)_{CAL} = -\frac{X_1 X_2 \ln\left[\mathrm{EXP}\left(-\frac{A_{12}}{RT}\right)\mathrm{EXP}\left(-\frac{A_{21}}{RT}\right)\right]}{\left[X_1 + X_2\left(\frac{V_2}{V_1}\right)\mathrm{EXP}\left(-\frac{A_{12}}{RT}\right)\right]\left[X_2 + X_1\left(\frac{V_1}{V_2}\right)\mathrm{EXP}\left(-\frac{A_{21}}{RT}\right)\right]}$$

Effective Wilson (Sabarathinam et al., 1977)

$$\Lambda_{12} = \frac{V_2}{V_1}\mathrm{EXP}\left(-\frac{A_{12}}{RT}\right); \qquad \Lambda_{21} = \frac{V_1}{V_2}\mathrm{EXP}\left(-\frac{A_{21}}{RT}\right); \quad \text{and}$$

$$\left(\frac{G^E}{RT}\right)_{CAL} = X_1 \ln\left(X_1 + X_2\Lambda_{21}\right) + X_2 \ln\left(X_2 + X_1\Lambda_{12}\right)$$

Modified Wilson (Huang-Lee) (Huang and Lee, 1996)

$$\tau_{12} = \mathrm{EXP}\left(-\frac{A_{12}}{RT}\right); \quad \tau_{21} = \mathrm{EXP}\left(-\frac{A_{21}}{RT}\right); \quad R_1' = \left(\frac{V_1}{V_2}\right)^{1/3},$$

$$R_2' = \left(\frac{V_2}{V_1}\right)^{1/3}; \quad \Phi_1' = \frac{X_1 R_1'}{X_1 R_1' + X_2 R_2'}; \quad \Phi_2' = \frac{X_2 R_2'}{X_1 R_1' + X_2 R_2'};$$

and

$$\left(\frac{G^E}{RT}\right)_{CAL} = -X_1 R_1' \ln\left(\Phi_1' + \Phi_2'\tau_{12}\right) - X_2 R_2' \ln\left(\Phi_2' + \Phi_1'\tau_{21}\right) + X_1 \ln\left(\frac{\Phi_1'}{X_1}\right) + X_2 \ln\left(\frac{\Phi_2'}{X_2}\right)$$

T. K. Wilson (Tsuboka and Katayama, 1975)

$$\tau_{12} = \frac{V_2}{V_1}\mathrm{EXP}\left(-\frac{A_{12}}{RT}\right); \quad \tau_{21} = \frac{V_1}{V_2}\mathrm{EXP}\left(-\frac{A_{21}}{RT}\right);$$

and

$$\left(\frac{G^E}{RT}\right)_{CAL} = X_1 \ln\left(\frac{X_1 + \left(\frac{V_2}{V_1}\right)X_2}{X_1 + X_2\tau_{12}}\right) + X_2 \ln\left(\frac{X_2 + \left(\frac{V_1}{V_2}\right)X_1}{X_2 + X_1\tau_{21}}\right)$$

Optimization methods

The brief details of the eight optimization methods used in this study are given below. All the optimization methods used are search methods and they do not require any derivative information during the calculation procedure.

Hooke-Jeeves method (HOOK)

In this method, an initial step size is chosen and the search is initiated from a given point. The method involves steps of exploration and pattern search. The step size *s* may be chosen in the range 0.05 to 1. Values beyond 1 can be tried; exploration about a point y: Let x = y. If e_i is unit vector along the coordinate

direction x, then the function is evaluated at $x + se_i$. If the function reduces, then x is updated to be $x + se_i$. If function does not reduce, then the function is evaluated at $x-se_i$. If the function reduces, then x is updated to be $x-se_i$. If both fail, the original x is retained. The searches are performed with i ranging from 1 to n. At this stage, the initial point is at y and the new point is at x. Exploration is said to be successful if the function value at x is lower than the value at y by a predetermined amount.

Powell's method (POWE)

Powell developed an idea of constructing the conjugate directions without using derivatives. After searching along all conjugate directions, a spacer step is introduced where a search is made from the current point along the coordinate directions. This is to ensure convergence. If a stage starts from point x^1 and ends at point x^2, then the convergence is said to be achieved when the norm $|x^2 - x^1|$ is less than a small parameter ε or by checking the function improvement from x^1 to x^2.

Rosenbrock's method (ROSE)

In Rosenbrocks method, the search is carried out in n orthogonal directions at any stage. New orthogonal directions are established for the next stage. The orthogonal setting makes this method robust and efficient. In this algorithm, the steps are taken in cyclic manner and repeated until there is at least one success and one failure in each direction.

Nelder-Mead simplex method (NELD)

In this simplex method, in an n-dimensional space n + 1 points form a simplex. A triangle is an example of a simplex in two dimensions. In three dimensions, a tetrahedron (four points) forms a simplex. An initial simplex in n dimensions is easily created by choosing the origin as one corner and n points, each marked at a distance from the origin along the coordinate axes. During the computation the operations of reflection and contraction (expansion) are performed on the simplex till the optimum is reached.

Cyclic coordinate search (CYCL)

In this method, the search is conducted along each of the coordinate directions for finding the minimum. If e_i is the unit vector along the coordinate direction i, we determine the value α_i minimizing $f(\alpha) = f(x + \alpha e_i)$, where α is a real number. A move is made to the new point $x + \alpha_i e_i$ at the end of the search along the direction i. In an n-dimensional problem, we define the search along all the directions as one stage. The function value at the end of the stage is compared to the value at the beginning of the stage in establishing the convergence. The length of the move at each stage is another parameter for convergence consideration. The search for the minimum in each direction follows the steps of the establishment of a three-point pattern and the search for the minimum in the interval established.

Random search (RAND)

Random Search through probability algorithm (RSPA) uses probabilities to guide search for an optimal solution. The role of left digit is more important than the role of right digit for evaluating objective function. We calculated probabilities for searching correct values of digits from left digits to right digits of every variable. The complexity of RSPA of a problem is not based on type of expressions in objective function or constraints (linear or nonlinear), but on the relation of decided variables in the formula of object function or constraints; therefore if there are k dependent variables, we select k variables to change the value of variables for every iteration. We cannot calculate exactly a number of iterations for searching an optimal solution because RSPA is a random algorithm; therefore we use unfixed number of iterations which has capability to find an optimal solution.

Simulated annealing (SIMA)

Generally we seek to update a point when the function has a lower value in the conventional methods of minimization and this strategy may lead to a local minimum. Simulated annealing is a method seeking global minimum by adopting a strategy where a higher value of a function is acceptable under some conditions. The analogy with annealing process where stresses are relived from a previously hardened body has been observed by Metropolis that the probability of higher energy is larger at higher temperatures and there is some chance of a high energy as the temperature drops. Energy in the annealing process some times increases even while the trend is a net decrease. This property applied to optimization problems is referred to as the Metropolis algorithm.

Genetic algorithm (GENE)

The genetic algorithm is a technique that draws its analogy from nature, and it simulates the evaluation process. This algorithm revolves around the genetic reproduction process and survival of the fittest strategies. The various steps in applying algorithm are: creation of initial population, evaluation, Creation of a meeting pool, cross over operation, mutation and evaluation.

RESULTS AND DISCUSSION

The binary system 2-Butanol-Tetrachloroethene at 101.08 kPa is chosen as an example system. The experimental data for this system show positive deviations from Roult's law and exhibit a minimum boiling azeotrope. The results of processing the isobaric binary vapor liquid equilibrium data of the above system to make a comparative study of five variants of Wilson G^E models and eight methods of optimization for estimating the parameters of the models are presented in Table 1. While processing the data with the various G^E models, the vapor phase is taken to be ideal. The molar volumes of the components are calculated using the modified Racket (1970) equation. The absolute average deviation between the experimental and calculated G^E/RT values and vapor compositions for each model and for each method of optimization are shown. The parameters of the selected variants of the Wilson model are also presented.

As can be observed from the values of Δy, all the variants of Wilson model selected for this study are satisfactorily describing the experimentally observed data. The lowest deviation (Δy) is observed with the Effective Wilson model. The calculated vapor composition by the Effective Wilson model using the eight

Table 1. Absolute average deviation in G^E/ RT, y and parameter values for each model, system: 2-butanol-tetracholoroethene pressure at 101.08 kPa.

Model	Optimization Method	$\Delta G^E/RT$	Δy	A_{12} (j/mol)	A_{21} (j/mol)
Wilson	Hooke and Jeeves	0.004249	0.004143	1426.757	3395.993
	Powell	0.004236	0.004139	1458.596	3425.231
	Rosenbrock	0.004239	0.004138	1455.541	3427.840
	Nelder Mead simplex	0.004223	0.004146	1472.358	3404.644
	Cyclic Coordinate	0.004239	0.004134	1456.724	3426.736
	Random search	0.004240	0.004134	1455.908	3427.725
	Simulated Annealing	0.004236	0.004126	1460.929	3421.765
	Genetic algorithm	0.004240	0.004134	1455.975	3427.643
Enthalpic Wilson	Hooke and Jeeves	0.004116	0.004514	666.4464	1996.071
	Powell	0.004114	0.004577	660.3227	2002.525
	Rosenbrock	0.004122	0.004529	659.5076	2003.082
	Nelder Mead simplex	0.004147	0.004288	660.0463	2002.989
	Cyclic Coordinate	0.004115	0.004521	663.8833	1998.722
	Random search	0.004120	0.004527	660.6419	2001.926
	Simulated Annealing	0.004122	0.004508	661.3513	2001.672
	Genetic algorithm	0.004120	0.004525	661.1623	2001.425
Effective Wilson	Hooke and Jeeves	0.004072	0.004100	-1896.929	-1538.071
	Powell	0.004102	0.004052	-1921.426	-1515.730
	Rosen brock	0.004071	0.004101	-1896.496	-1538.460
	Nelder Mead simplex	0.004101	0.004196	-1900.522	-1532.090
	Cyclic Coordinate	0.004062	0.004103	-1891.247	-1543.402
	Random search	0.004071	0.004096	-1896.718	-1538.452
	Simulated Annealing	0.004058	0.004069	-1893.628	-1542.497
	Genetic algorithm	0.004071	0.004096	-1896.779	-1538.383
Modified Wilson	Hooke and Jeeves	0.004212	0.004228	1962.571	2920.429
	Powell	0.004212	0.004275	1955.128	2928.496
	Rosenbrock	0.004219	0.004226	1955.581	2929.923
	Nelder Mead simplex	0.004220	0.004192	1960.406	2926.663
	Cyclic Coordinate	0.004215	0.004237	1958.415	2925.172
	Random search	0.004215	0.004237	1957.929	2925.783
	Simulated Annealing	0.004212	0.004261	1957.702	2923.799
	Genetic algorithm	0.004215	0.004240	1957.943	2925.479
T. K. Wilson	Hooke and Jeeves	0.004195	0.004270	2408.562	2417.438
	Powell	0.004185	0.004250	2428.834	2393.785
	Rosenbrock	0.004187	0.004252	2419.698	2404.217
	Nelder Mead simplex	0.004207	0.004232	2402.560	2427.461
	Cyclic Coordinate	0.004188	0.004255	2417.793	2406.445
	Random search	0.004187	0.004252	2419.629	2404.306
	Simulated Annealing	0.004209	0.004055	2414.197	2410.280
	Genetic algorithm	0.004187	0.004252	2419.634	2404.300

optimization methods are presented in Table 2. As can be observed from the results, all the optimization methods selected for this study are equally good for describing the VLE data of the example system. The graphical representation of the deviation between the experimental and the calculated vapor composition of the

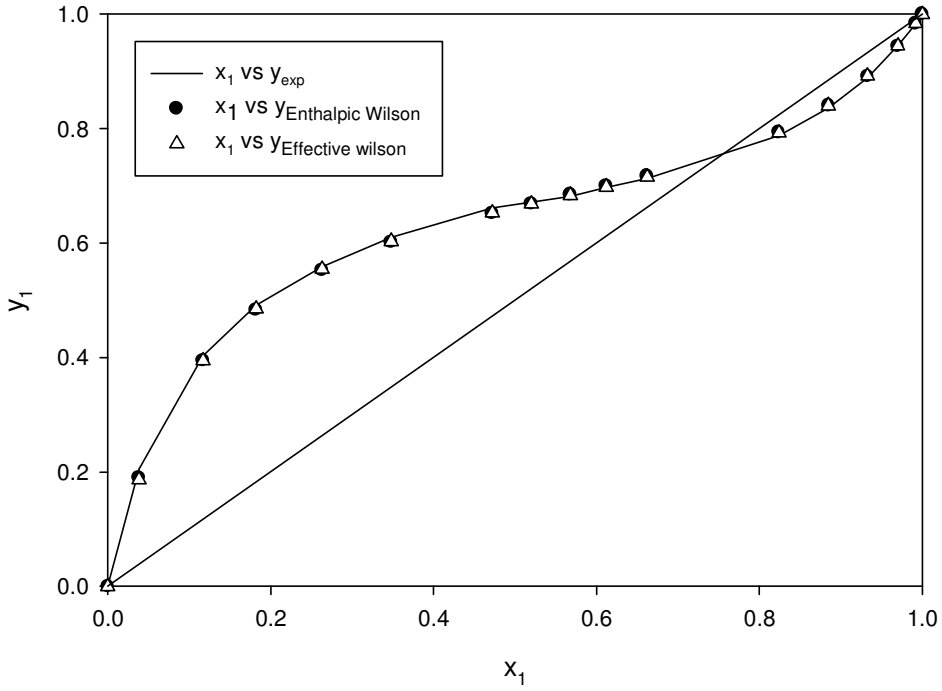

Figure 1. Comparison of vapour composition using enthalpic and effective Wilson thermodynamic models for the system: 2-butanol-tetrachloroethene at 101.08 kPa.

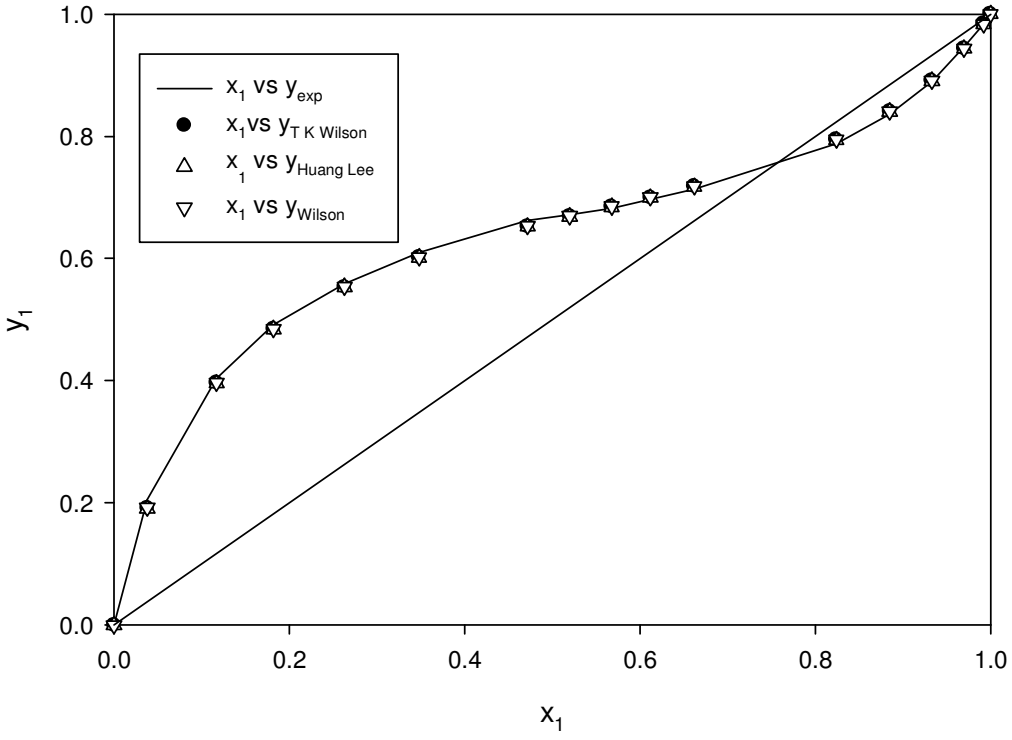

Figure 2. Comparison of vapour composition using Wilson, T. K. Wilson and Modified Wilson thermodynamic models for the system 2- butanol-tetrachloroethene at 101.08 kPa.

Enthalpic and Effective Wison model is shown in Figure 1. The optimization method chosen is Hook and Jeeves for the study. Figure 2 is representing the deviations of vapor composition using Wilson, Modified Wilson and T.

Table 2. Calculated vapor composition by Effective Wilson equation, system: 2-butanol-tetracholoroethene at 101.08 kPa.

T	x_1	y_1	y_1 Calculated			
			HOOK	POWE	ROSE	NELD
394.250	0.000	0.000	0.000000	0.000000	0.000000	0.000000
387.650	0.038	0.205	0.191899	0.192327	0.191901	0.191915
380.250	0.117	0.403	0.396964	0.397372	0.396974	0.396996
376.650	0.182	0.491	0.485309	0.485537	0.485326	0.485347
374.050	0.263	0.559	0.553854	0.553869	0.553876	0.553894
372.550	0.348	0.610	0.601642	0.601490	0.601665	0.601680
371.350	0.472	0.662	0.651066	0.650777	0.651086	0.651094
370.950	0.520	0.672	0.667153	0.666842	0.667170	0.667175
370.550	0.568	0.682	0.682698	0.682383	0.682712	0.682714
370.350	0.612	0.697	0.697293	0.696989	0.697303	0.697302
370.250	0.662	0.713	0.714944	0.714669	0.714948	0.714943
370.250	0.824	0.788	0.792467	0.792402	0.792450	0.792434
370.750	0.885	0.836	0.839820	0.839855	0.839797	0.839778
371.350	0.933	0.889	0.891231	0.891321	0.891209	0.891192
371.650	0.970	0.946	0.944104	0.944185	0.944089	0.944078
372.450	0.992	0.984	0.983756	0.983787	0.983751	0.983748
372.650	1.000	1.000	1.000000	1.000000	1.000000	1.000000

T	x_1	y_1	y_1 Calculated			
			CYCL	RAND	SIMA	GENE
394.250	0.000	0.000	0.000000	0.000000	0.000000	0.000000
387.650	0.038	0.205	0.191711	0.191903	0.192007	0.191904
380.250	0.117	0.403	0.396819	0.396972	0.397111	0.396972
376.650	0.182	0.491	0.485270	0.485320	0.485443	0.485319
374.050	0.263	0.559	0.553931	0.553866	0.553962	0.553865
372.550	0.348	0.610	0.601801	0.601653	0.601719	0.601652
371.350	0.472	0.662	0.651276	0.651075	0.651097	0.651073
370.950	0.520	0.672	0.667363	0.667160	0.667166	0.667158
370.550	0.568	0.682	0.682897	0.682703	0.682692	0.682702
370.350	0.612	0.697	0.697471	0.697297	0.697271	0.697295
370.250	0.662	0.713	0.715087	0.714944	0.714901	0.714943
370.250	0.824	0.788	0.792431	0.792458	0.792369	0.792459
370.750	0.885	0.836	0.839713	0.839807	0.839715	0.839809
371.350	0.933	0.889	0.891100	0.891220	0.891140	0.891221
371.650	0.970	0.946	0.944006	0.944096	0.944047	0.944097
372.450	0.992	0.984	0.983722	0.983754	0.983738	0.983754
372.650	1.000	1.000	1.000000	1.000000	1.000000	1.000000

K .Wilson. From the figures, it is clearly evident that both the models are correlating and the experimental data vary accurately.

Conclusion

The comparative evaluation of five variants of Wilson model and eight optimization methods for describing the VLE of 2-butanol-tetrachloroethene is presented. Effective Wilson model is found to produce the best agreement with the experimental data for the selected system.

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