**Reply to the comments “On the consistency and correctness of thermodynamics phase equilibria modeling and correlation reports published in Fuel journal”**

It is appreciating that the audience of FUEL Journal tried to reconsider their works [1, 2] in accord with the presented note [3] which aimed to indicate wherever a practical use of phase equilibrium data is sought (i.e. forecasting of equilibrium phases), it is necessary to check the thermodynamic model's parameters completely to reduce the possible errors.

However, for just correlating or fitting of the experimental data to some mathematical expressions (as the form of NRTL model), the application of model without considering the closure equation might be fair. We are trying to note that this way, doing some mathematical calculation without any thermodynamic basis, is not recommended [[1]](#endnote-1).

Mejía and Segura claimed [1] that they implemented the closure equation in their work [2] to show that the reported binary interaction parameters without the closure equation are not thermodynamically meaningless. It has been warily mentioned that the implementation of closure equation slightly improved the model’s performance and same conclusion obtained as in their original paper[2].

There are some issues with such re-calculation and conclusion. In their works [1, 2], the method of division of data points to test and validation sets was not explained. Their study was carried out in isobaric condition [2] where the temperature dependency of binary interaction parameters prevails and must be considered [4, 5]. Furthermore, the method of phase equilibrium calculation, which ends to the determination of these parameters, has not been presented.

They just fitted the experimental data to a mathematical expression with the functional form as of NRTL model and tried to find the best regression of data [2] (correlative approachi). it is a pure mathematical calculation in which no thermodynamic understanding of process could be established. As Wisniak et al., said, “computer and curve fitting software do not know thermodynamics” [5].

As the results of their calculations show, the mathematical expressions (i.e. models) are appropriate. The application of full set of model equations (i.e. NRTL with closure equation) provides better representation of the experimental data, which itself must be interpreted as if the models are appropriate for the system of under study.

There is no guarantee that the implementation of closure equation will end to better regression. For example, there would be a system for which, the application of NRTL model would not be the good choice for representation of phase behavior, and the worst result would be obtained for full set of equations. The slightly improvement in the calculations results should not interpreted so that the binary interaction parameters without the implementation of closure have thermodynamically meaning, or the closure equation is redundant or to overlook the phase behavior.

It’s true that the action and reaction mechanical principle, as mentioned in [1], can also be used to obtain closure equation, however, without implemented of such assumption or mechanism, also, one might obtain this equation i. We failed to find a connectivity between the studies referred in[1] and the fact which might probably violates the existence of closure equation.

The effect of attractive term and combining rule were studied by Nakanishi and Toukubo [6]. They concluded that the random mixing rule reveals better agreement to the experimental data and difference of unlike interaction is reflected quite well by the internal energy and radial distribution function (RDF). One might intuitively interpret this conclusion as the importance of the parameters as some thermodynamic characteristics of the system, while in almost all of the cited papers in [3, 7], they were treated as some statistical and pure mathematical numbers.

Abusleme et al., [8] attempted to show the possibility of obtaining Local Composition (LC) values of Léonard-Jones (LJ) model mixtures by computer simulation considering the radial distribution functions. The main purpose was the discussion of the effect of non-Lorentz-Berthelot mixing rules on the LC, and obtaining a correlation for LC using a Wilson type equation [8].

They concluded that the dependency of LC to strength of attractive interaction in Wilson original equation is valid for models with large attractive interaction difference [8]. Models with minor attractive interaction difference result in larger LCs of two components than the overall compositions [8], thus prediction of LC by direct use of the Wilson and related equations will not be successful.

For the studied system in [1], If there’s minor attractive interaction difference between system components, so the used models might not be “appropriate” and one would not be able to assure the reliability of models for thermodynamic calculations. On the other hand, if these differences were large, consequently, the use of Wilson and its related equation would be appropriate which require the implementation of closure equation [6, 8].

By assessing the method of calculation, objective functions and their minimization procedures, Sørensen et al., [9] studied the liquid-liquid equilibria correlation using models for phase equilibrium calculation. Determination of binary interaction parameters were investigated for the case of (i) searching of all six binary interaction parameters and (ii) fixing of one or some of the binary interaction parameters and searching the remaining [9].

The fixing of these parameters in the latter case might be in the form of the assigning a value to one and searching the other binary interaction parameters, or the one with assigned value might has the possibility of varying. The latter would be acceptable but for the first, there would be argument. As Sahoo et al. noted [10, 11], fixing of one or some of the binary interaction parameters would suffer from the fixing step, as the fixed binary interaction parameter is an arbitrary one with five deferent possibility. The work of Sahoo et al. [10, 11] would give better understandings regarding to the closure equation if a coding/decoding free algorithm was employed.

Varhegyi and Eon [12] entirely carried out a purely mathematical study to find the best fit and no attempt were taken to discern the physical meaning of the calculated parameters (mathematical calculation in contrast to thermodynamic calculation) [12]. This approach cannot be regarded as an appropriate way for the phase equilibrium calculation; however, for the case of experimental data consistency test it would be acceptable.

Regarding to the Eq. 2 in the note by Mejía and Segura [1]., it must noted that the closure equation or the NRTL model’s boundary condition holds among these binary interaction parameters and intuitive interpretation of these parameters for systems with more than two-component is not allowed i.

In chemical thermodynamic point of view, the Gibbs–Duhem equation is the only reliable tool for the evaluation of thermodynamic consistency of models [13]. However, the Gibbs–Duhem equation does not violate the existence of closure equation and models, with and without closure equation, satisfy the Gibbs–Duhem equation.

**References**

1. Mejía, A. and H. Segura, *Comments “On the consistency and correctness of thermodynamics phase equilibria modeling and correlations reports” [Fuel (submitted for publication)].* Fuel, 2014(0).

2. Mejía, A., H. Segura, and M. Cartes, *Phase equilibria and interfacial tensions in the systems ethanol+2-methoxy-2-methylbutane+hexane.* Fuel, 2014. **117**: p. 996-1003.

3. Asgarpour Khansary, M. and M.A. Aroon, *On the consistency and correctness of thermodynamics phase equilibria modeling and correlation reports published in Fuel journal.* Fuel, 2014(0).

4. John M. Prausnitz, Rudiger N. Lichtenthaler, and Edmundo Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria* 3ed. 1998: Prentice Hall.

5. Wisniak, J., A. Apelblat, and H. Segura, *An Assessment of Thermodynamic Consistency Tests for Vapor-Liquid Equilibrium Data.* Physics and Chemistry of Liquids, 1997. **35**(1): p. 1-58.

6. Toukubo, K. and K. Nakanishi, *Molecular Dynamics Studies of Lennard-Jones Liquid Mixtures. III. Structural and Thermodynamic Properties of Several Equimolar Mixtures.* Berichte der Bunsengesellschaft für physikalische Chemie, 1977. **81**(10): p. 1046-1048.

7. Alvarez Juliá, J., et al., *On the application of the NRTL method to ternary (liquid+liquid) equilibria.* The Journal of Chemical Thermodynamics, 2005. **37**(5): p. 437-443.

8. Abusleme, J.A., K. Nakanishi, and J.H. Vera, *Local composition in ternary Lennard-Jones liquid mixtures: molecular dynamics simulation and a simple correlation.* Fluid Phase Equilibria, 1990. **58**(1–2): p. 81-92.

9. Sørensen, J.M., et al., *Liquid—liquid equilibrium data: Their retrieval, correlation and prediction Part II: Correlation.* Fluid Phase Equilibria, 1979. **3**(1): p. 47-82.

10. Sahoo, R.K., et al., *Improved binary parameters using GA for multi-component aromatic extraction: NRTL model without and with closure equations.* Fluid Phase Equilibria, 2006. **239**(1): p. 107-119.

11. Sahoo, R.K., T. Banerjee, and A. Khanna, *UNIQUAC Interaction Parameters with Closure for Imidazolium Based Ionic Liquid Systems Using Genetic Algorithm.* The Canadian Journal of Chemical Engineering, 2008. **85**(6): p. 833-853.

12. Varhegyi, G. and C.H. Eon, *Calculation of the Free Energy Equation Parameters from Ternary Liquid-Liquid Equilibrium Data.* Industrial & Engineering Chemistry Fundamentals, 1977. **16**(2): p. 182-185.

13. J.M. Smith, H.V.N., Michael Abbott, *Introduction to Chemical Engineering Thermodynamics*. 7 ed. 2005: McGraw-Hill.

1. The second part submitted as letter to the editor. [↑](#endnote-ref-1)