**On The Consistency and Correctness of Thermodynamics Phase Equilibria Modeling and Correlation Reports Published In FUEL Journal**

Thermodynamic calculation can be regarded as a powerful tool for assessment of the experimental data correctness. Using such calculations, prediction and estimation can be done prior to any experimental investigations to avoid the cost and time needed to obtain basic experimental data. In phase equilibrium calculations, various thermodynamics models, e.g. equation of states (EOS) and activity coefficient models **(**such asNRTL, UNIQUAC, Margules, van Laar and etc.**)**, can be used with regard to the system of under study. Among different activity coefficient models, **NRTL** (Eq. 1) and **UNIQUAC** (Eq. 2) correlations are used extensively due to their reliable predictions [1-2].

 (1)

Here - are the binary interaction parameters and αij is the non-randomness parameter.

The **UNIQUAC** model is given by **Eq. 2**;

 (2)

Here, are the binary interaction parameters of the model.

For **UNIQUAC** and **NRTL** models, the binary interaction parameters are not independent of each other. In fact, the dependency of these parameters follows a linear relationship called closure equation as reported in Refs. [**2-4**].

For a ternary system, following closure equation (**Eq. 3**) must be held on binary interaction parameters of **NRTL** model [**5**];

 (3-1)

 (3-2)

Similarly, for the **UNIQUAC** model, one would obtain a relationship among as Eq. 3-1.

This equation (Eq. 3-1) provide, to the interaction parameters, a meaningful calculation method and strategy. In other words, in phase equilibrium calculations, one must constrain the numerically calculated interaction parameters to satisfy****. It must be noted that one may find a set of optimum interaction parameters without the implementation of equation **2** (as seen in the papers referred here), but these values are thermodynamically meaningless and their use for calculation of equilibrium point would be risky. Here the most recent reports[[1]](#footnote-1) published in FUEL Journal that deal with the phase equilibrium calculations, have been studied to check their adherence to **Eq. 3-1**.

The authors of the Ref. [**6**] reported Liquid–liquid equilibrium for ternary systems containing ethylic palm oil biodiesel + ethanol + glycerol and palm oil biodiesel + ethanol + water. The ternary systems, at temperatures of 298.15 and 323.15 K and atmospheric pressure, were modeled thermodynamically using **NRTL** model. They have reported that their correlations give good agreement to the experimental data.

The ternary system of ethanol + 2-methoxy-2-methylbutane + hexane at 94 kPa and in the temperature range 331–350 K has been studied in Ref. [**7**] where three Gibbs excess (GE) models of **UNIQUAC**, **NRTL** and **Wilson** was used for thermodynamics calculations. Equilibrium data of the ternary were well-predicted using mentioned models.

The **NRTL** and **UNIQUAC** activity coefficient models were used to correlate the Liquid–liquid equilibrium data of systems containing Brazil nut biodiesel + methanol + glycerin at 303.15 K and 323.15 K in Ref. [**8**] and the results were reported are in good agreement with the experimental data.

For the methanol + glycerol + methyl oleate systems, in Ref. [9], two models of **NRTL** and **UNIQUAC** have been used. They also studied the performance of **ASOG**, **UNIFAC**, **UNIFAC**-**LLE** and **UNIFAC** Dortmund activity models in their research.

For three systems of water + ethanol + FAEE from crambe oil, water + ethanol + FAEE from fodder radish oil, and water + ethanol + FAEE from macauba pulp oil, the **NRTL** and **UNIQUAC** activity coefficient models were used to correlate experimental data [**10**]. These thermodynamic models properly described the **LLE** of these systems resulting in average deviation ranging from 0.49% to 1.29%.

**Table 1** summarizes all the binary interaction parameters of the cited references together with the calculated value of closure equation for each system. The interesting point is that the closure equations are not satisfied and large deviation values are observable. In fact, the authors only tried to fit the experimental data to some model. It must be noted that those reported binary interaction parameters can only be used for correlation in the range of determinations (the point used for their calculations).

(insert **Table 1** here)

Although these binary interaction parameters are in good agreement with experimental data but they are thermodynamically nonsense and present no physical meaning. For a thermodynamically correct calculation, the closure equation - () must be taken into account in numerical calculations. Therefore, it is very risky to use the binary interaction parameters for equilibrium data calculations without considering the closure equation () as a check point.

**References**

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1. The "NRTL" phrase used as the keyword for searching purpose. [↑](#footnote-ref-1)