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Correlation of interaction parameters in Wilson, NRTL and UNIQUAC models using theoretical methods

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ABSTRACT

The activity coefficient models of Wilson, Nonrandom Two Liquid Theory (NRTL) and Universal Quasi-chemical Theory (UNIQUAC) are of the most applied chemical thermodynamic models in phase equilibria calculations and materials behavior prediction and/or correlation. The reliable and accurate evaluation and determination of interaction/adjustable parameters defined in these models, which are necessary for any future applications of models in binary and multicomponent systems, requires the knowledge on experimental data of binary systems. By using such experimental data and regression and fitting of data, in literature, these interaction parameters are obtained for a substantial number of systems. Here, a new theoretical methodology has been developed and examined for estimation of these parameters without the use of experimental data. The presented method equates the activity coefficients calculated by a Compressible Regular Solution Theory (CRS) to those calculated using the three aforementioned models and the interaction parameters are obtained by optimally solving the constructed system of equations. For CRS theory, the application of Sanchez and Lacombe Equation of State (LS-EoS), Constantinou and Gani Group Contribution Method and Hoftyzer and van Krevelen Group Contribution Method was considered while for models of Wilson, NRTL and UNIQUAC, the interaction parameters were searched by implementation of an evolutionary optimization technique. The obtained results are compared to those reported in literature and desirable agreement was found. The method is simple, fast, implementable in computer routines; straightforward and accurate and can be used to estimate these binary interaction parameters for systems of interest. Some phase calculations are also included to demonstrate the applicability of method.

1. Introduction

For prediction/correlation of thermodynamic properties such as equilibrium compositions, it's required to employ a reliable thermodynamic model based on the considered system and process. The activity coefficient models of Wilson, Nonrandom Two-Liquid Theory (NRTL) and Universal Quasi-chemical Theory (UNIQUAC) are of most applied models used for thermodynamic study of a substantial number of binary and multicomponent systems as they are able to properly represent behavior of non-ideal mixtures [1,2]. These chemical thermodynamic models have some interaction parameters that require the availability and knowledge on experimental data of systems to be adjusted and made the model ready for further thermodynamic calculations. By determination of these interaction parameters from binary systems data, it's possible to employ them for property calculations of multicomponent systems that are composed/formed of these binaries [1,2].

For constituent binary systems, the calculated/determined interaction parameters could have physical interpretations, for example in Wilson activity coefficient model, the interaction parameters are related to the pure component molar volumes and characteristic energy differences. However, in practical applications and uses, the systems of interest are multicomponent or multiphase systems [1,2], for which the constituent binary systems

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data might not be accessible. For such systems, the mixture/solution data are used to calculate interaction parameters numerically by mathematical fitting and regression of data to the models equations aiming to minimize the deviations between model calculations and experimental data. Although numerical values can be obtained by such calculations, however, we're not then allowed to interpret these values physically. The calculated interaction parameters, in this case, are some correlative parameters that can be used only for reproduction of data using thermodynamic model [2–7].

To be more specific, the calculation of binary interaction parameters from ternary (or multicomponent) systems is nothing more than data fitting practice, in where the mathematical function is the main equations of thermodynamic models and unknowns are the interaction parameters. It means that we would be able to check the goodness of any arbitrary mathematical function by fitting of experimentally measured data to the function and searching for its optimal coefficients and agreement to the available data. Thus, it must be of interest to develop an alternative method to calculate or at least to obtain an estimate of such data that are thermodynamically meaningful as investigated in this work and illustrated in following sections.

2. Proposed methodology and method of implementation

In literature [1,2], the activity coefficient models of Wilson, NRTL and UNIQUAC are introduced together with their main equations. The required methods and models including Compressible Regular Solution Theory (CRS) [8], Sanchez and Lacombe Equation of State (LS-EoS) [9], Constantinou and Gani Group Contribution Method [10], Hoftyzer and van Krevelen Group Contribution Method [11] are provided and illustrated elsewhere [11,12]. The reader is advised to read these reference works and then refers to the proposed method.

The basic idea here is employing the Compressible Regular Solution Theory (CRS) model first to calculate the activity coefficients (chemical potentials) of components (as predictive activity model), and then equating this calculated value, by replacing the obtained value in left side of equations provided for Wilson, NRTL and UNIQAUC i.e. $[\ln \gamma_i]^{Wilson} = [\ln \gamma_i]^{CRS}$, $[\ln \gamma_i]^{NRTL} = [\ln \gamma_i]^{CRS}$ and $[\ln \gamma_1]^{UNIQUAC} = [\ln \gamma_1]^{CRS}$ respectively, where on the right sides of obtained equations, the unknown sets are the binary interaction parameters $\{\Lambda_{12},\Lambda_{21}\}$, $\{\tau_{12},\tau_{21}\}$ and $\{\tau_{12},\tau_{21}\}$ for Wilson, NRTL and UNIQUAC models respectively. This way, a system of n equations would be obtained for an n component system, where the unknowns are the binary interaction parameters of the models.

For example, in Wilson model, for a binary system (two-component solution), one can write;

$$[\ln \gamma_1]^{Wilson} = -\ln[x_1 + x_2\Lambda_{12}] + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right] = [\ln \gamma_1]^{CRS} \quad (1)$$

$$[\ln \gamma_2]^{Wilson} = -\ln[x_2 + x_1\Lambda_{21}] - x_1\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right] = [\ln \gamma_2]^{CRS} \quad (2)$$

On the right sides of these equations, the unknown sets are $\{\Lambda_{12},\Lambda_{21}\}$ for Wilson model. The procedure is the same for other two models. For NRTL model, one can write;

$$[\ln \gamma_1]^{NRTL} = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] = [\ln \gamma_1]^{CRS} \quad (3)$$

$$[\ln \gamma_2]^{NRTL} = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] = [\ln \gamma_2]^{CRS} \quad (4)$$

And for UNIQUAC model, one can write;

$$[\ln \gamma_1]^{UNIQUAC} = \ln\frac{\Phi_1^*}{x_1} + \frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1^*} + \Phi_2^*\left[l_1 - \frac{r_1}{r_2}l_2\right] - q_1'\ln[\theta_1' + \theta_2'\tau_{21}]\cdots + \theta_2'q_1'\left[\frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}}\right] = [\ln \gamma_1]^{CRS} \quad (5)$$

$$[\ln \gamma_2]^{UNIQUAC} = \ln\frac{\Phi_2^*}{x_2} + \frac{z}{2}q_2\ln\frac{\theta_2}{\Phi_2^*} + \Phi_1^*\left[l_2 - \frac{r_2}{r_1}l_1\right] - q_2'\ln[\theta_2' + \theta_1'\tau_{12}]\cdots + \theta_1'q_2'\left[\frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}}\right] = [\ln \gamma_2]^{CRS} \quad (6)$$

On the right sides of these equations, the unknown sets are $\{\tau_{12},\tau_{21}\}$ and $\{\tau_{12},\tau_{21}\}$ for NRTL and UNIQUAC models.

For multicomponent systems, simply the constituent binaries of systems must be constructed and the method described for binary systems must be followed for each binary. To reduce any redundant computational cost, the application of closure equation is advised [3–7,13,14]. All the calculations are requested to be restricted on binary systems and constituent binaries of multicomponent systems in order to have some physical interpretation of obtained numeric values.

Such systems of equations are nonlinear with respect to the unknowns and direct calculation of these unknowns seems to be impossible. This limitation requires the application of mathematical techniques such as iterative regression. However, thanks to recent advances in computational science, the calculation and determination of these unknowns is not a challenging work due to availability of computers. The application of iterative techniques is time consuming and the calculated outputs might not be the real values as there might be local minima of considered objective functions. The most reliable, simple and advanced method of numerical solution of such system of equations is the application of an optimization algorithm, where the unknown sets (i.e.$\{\Lambda_{12},\Lambda_{21}\}$, $\{\tau_{12},\tau_{21}\}$ and$\{\tau_{12},\tau_{21}\}$) are searched against the criteria of least (and no) values obtained for the predefined objectives. Of the most common optimization algorithms in engineering applications are evolutionary and swarm intelligent-based techniques such as genetic algorithm and particle swarm optimization methods. Here, the particle swarm optimization (PSO) has been employed [15]. The method of searching for binary interaction parameters by PSO is the same as described in Ref. [15].

The steps of calculations are as described and listed below;

1. Draw desired components molecular structure and identify the each group/class of Boudouris et al. [10],