3^{rd} Project Report: Liquid-Liquid Equilibrium of Alkane/Sulfolane Binary Mixture by NRTL

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CHE 3006: Chemical Engineering Thermodynamics 2
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November 18, 2021

Abstract

In this report, a review of liquid-liquid equilibrium (LLE) is presented with local-composition models (Wilson equation, NRTL, and UNIQUAC/UNIFAC) and phase stability criterion for LLE is introduced. Experimental data of LLE for two binary systems containing sulfolane and one of alkanes (pentane and hexane) over the temperature range of 300 K to the upper critical solution temperature (UCST) were correlated using NRTL (non-random-two-liquid) model. The NRTL parameters were curve-fitted from experimental data and a new tau (τ) function with an added linear term is introduced to show improved accuracy compared to the function implemented by Aspen Institute. For NRTL calculation and parameter optimization, the same 'isoactivity' objective function was set to be minimized by simple search method.

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1 Introduction

The separation process is essential to obtain a necessary product with a high concentration in industrial process with mixture. The process of extraction and production of aromatic hydrocarbons by reforming naphtha produced in naphtha reforming process is called the BTX(**b**enzene-**t**oluene-**x**ylene) process [1], [2]. BTX can be obtained through sulfolane, BTU, PAREX, and ISOMAR processes. **Figure A** is a typical diagram of this process provided by Sweeney and Bryan [2, p. 10].

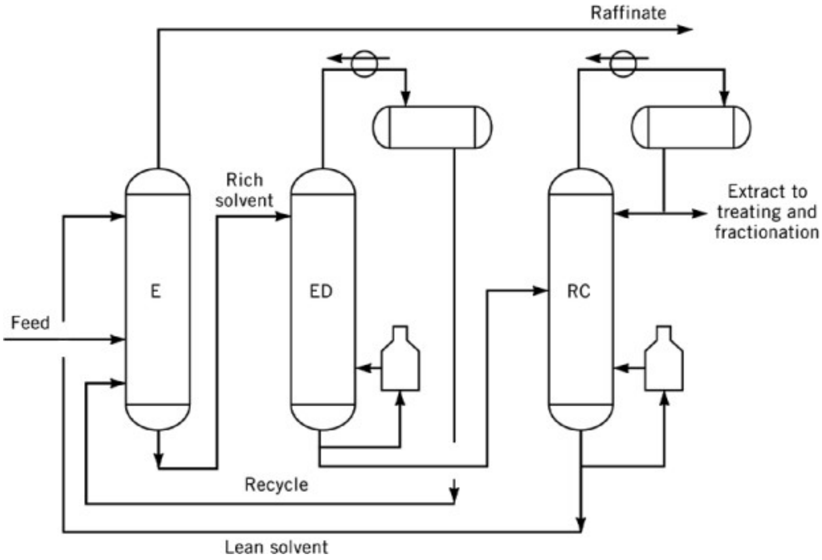


Figure A. Shell sulfolane extraction process. E, extraction; ED, extractive distillation; RC, recovery column. Courtesy of UOP, Inc.

The manufactured toluene is usually converted into benzene, which is commonly used as a raw material for styrene monomer (SM), nylon and cumene. The polyester film can be produced with para-xylene (PX) [3]. This project aims to study liquid-liquid equilibria (LLE) of alkanes contained in the raw material and the solvent in the sulfolane process. Various solvents including sulfolane, glycol and NFM (N-formylmorpholine) may be used in the sulfolane process [4], [5].

Before running the process, it is important to theoretically optimize the chemical process to determine the amount of solvent and raw material for appropriate scale of facilities and operating cost. In order to predict the behavior of each component in the solution, it is necessary to know the physical properties of the mixture in a LLE. Especially, an actual solution shows different behavior from ideal solution due to intermolecular interactions and non-randomness. Therefore, to make more precise and accurate calculation, it is necessary to understand thermodynamic properties of an actual solution and use appropriate formulas. Thermodynamic models for computing the properties of real solution include Wilson Equation, NRTL model, UNIQUAC and UNIFAC. As mentioned above, these models take into account the interaction and non-randomness between compositions. Each model simulates actual solution by introducing different set of parameters.

2 Theory

2.1 LLE (Liquid-Liquid Equilibrium)

An unexpected presence of two liquid phases can be a critical problem in distillation and pumping. Hence one must make sure by experiment or calculation, whether the solution is in single liquid phase or two or more liquid phases are present in the solution. Despite such practical importance in simulation of process, LLE has not received nearly as much attention as VLE (**v**apor-**l**iquid **e**quilibrium). There are several reasons for this [6]:

1) The experimental determination of LLE compositions can often be carried out on an ad hoc basis which reduces the incentive for correlation.
2) The correlation of LLE da can be, from numerical point of view, much more difficult than the correlation of VLE.
3) Temperature effects are more pronounced for LLE than for VLE.
4) Economically, distillation plays a bigger role in industry than does extraction.

Nevertheless, many references, especially experimental work, exist for LLE.

Like VLE, LLE satisfies the following condition with phase α and β at constant temperature. In this project, the effect of pressure on the behavior of LLE is negligible.

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \qquad (i(\text{species}) = 1, 2, \dots, N)$$

According to the definition of activity coefficient, $\gamma_i = \hat{f}_i^{\alpha}/x_i f_i$, the fugacity in each phase can be expressed as below.

$$x_i^{\alpha}\gamma_i^{\alpha}f_i^{\alpha} = x_i^{\beta}\gamma_i^{\beta}f_i^{\beta}$$

The fugacity of pure species i is $f_i^{\alpha} = f_i^{\beta} = f_i$ at constant temperature and pressure. So, under LLE conditions, the equation below is satisfied.

$$x_i^{\alpha}\gamma_i^{\alpha} = x_i^{\beta}\gamma_i^{\beta}$$

The activity coefficient depends on the composition, temperature and pressure. Therefore, for the binary solution, the activity coefficient can be measured with x_1, T, and P through the relation $(x_1 + x_2 = 1)$ [7, pp. 590–591].

2.2 Local-Composition Models

Theoretical developments for describing the molecular thermodynamics of liquid-solution behavior are often based on the concept of *local composition*. The ideal solution is a totally random mixture of constituent particles, so the concentration of the total solution and a certain portion of the solution are the same. However, in actual solution, the constituent particles are not evenly mixed like ideal solution, and local concentration of solution is different to entire concentration. Hence it is important to understand the concept of *local composition* in order to simulate the behavior of actual solutions [7, pp. 471–472]. To measure the properties of actual solutions in consideration of this concept, Wilson equation, NRTL equation, UNIQUAC(**Uni**versal **Qua**si **C**hemical), and UNIFAC (**UNI**QUAC **F**unctional group **Ac**tivity) can be used.

2.2.1 Wilson Equation

Wilson equation proposed by G. M. Wilson in 1964 can calculate the behavior of the solution through Λ_{12} and Λ_{21}.

$$\frac{G^E}{RT} = -\sum_i \left[x_i \ln \left(\sum_j x_i \Lambda_{ij} \right) \right]$$

$$= -[x_1 \ln(x_1\Lambda_{11} + x_2\Lambda_{12})\, x_2 \ln(x_1\Lambda_{21} + x_2\Lambda_{22})] \quad \text{(for a binary system)}$$

$$\therefore \frac{G^E}{RT} = -[x_1 \ln(x_1 + x_2\Lambda_{12}) + x_2 \ln(x_2 + x_1\Lambda_{21})] \quad (\because \Lambda_{11} = \Lambda_{22} = 1)$$

Equation 1. Wilson equation

By applying the relation between activity coefficient and excess Gibbs energy, activity coefficients are represented as following equations (detailed calculation procedure for Wilson equation is in **Appendix A.1**):

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

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

For infinite dilution ($x_1 \to 0$ or $x_2 \to 0$), these equations become:

$$\lim_{\substack{x_1\to 0\\(x_2\to 1)}} \ln\gamma_1 = \ln\gamma_1^\infty = -\ln\Lambda_{12} + 1 - \Lambda_{21}$$

$$\lim_{\substack{x_2\to 0\\(x_1\to 1)}} \ln\gamma_1 = \ln\gamma_2^\infty = -\ln\Lambda_{21} + 1 - \Lambda_{12}$$

A serious disadvantage of Wilson's equation lies in its inability to predict limited miscibility. When Wilson equation is substituted into the equations of thermodynamic stability for a binary system, no parameters Λ_{12} and Λ_{21} can be found that indicates the existence of two stable liquid phase. So, Wilson equation should be used only for liquid systems that are completely miscible or else for those limited regions of partially miscible solutions that only one liquid phase is present. Therefore, in this project, Wilson's equation not been adopted as actual liquid-liquid solution model [8, pp. 164–165].

2.2.2 NRTL(Non-Random-Two-Liquid) Model

NRTL model reflects the characteristics of the local composition of the actual solution.

$$\frac{G^E}{x_1x_2RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1G_{12}}$$

Equation 2. NRTL Equation

Here,

$$G_{12} = \exp(-\alpha\tau_{12}), G_{21} = \exp(-\alpha\tau_{21})$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij}lnT$$

By applying the relation between activity coefficient and excess Gibbs energy, activity coefficients are represented as following equations (detailed calculation procedure for Wilson equation is in **Appendix A.2**):

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

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{!2}}{x_2 + x_!G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{x_1 + x_2G_{21}}\right]$$

The infinite-dilution ($x_1 \rightarrow 0 \; or \; x_2 \rightarrow 0$) values of the activity coefficients are given by equations:

$$\lim_{x_1 \rightarrow 0 (x_2 \rightarrow 1)} \ln \gamma_1 = \ln \gamma_1^{\infty} = \tau_{21} + \tau_{12} G_{12} = \tau_{21} + \tau_{12} \exp\left(-\alpha \tau_{12}\right)$$

$$\lim_{x_2 \rightarrow 0 (x_1 \rightarrow 1)} \ln \gamma_2 = \ln \gamma_2^{\infty} = \tau_{12} + \tau_{21} G_{21} = \tau_{12} + \tau_{21} \exp\left(-\alpha \tau_{21}\right)$$

2.2.3 UNIQUAC/UNIFAC Method

The UNIQUAC equation calculates $g \equiv \frac{G^E}{RT}$ as the sum of the two terms. g^C is a combinatorial term, which is related to the different shape and size of molecules in the mixture. g^R is a residual term, which is different from residual Gibbs free energy defined as the difference between real and ideal Gibbs free energy, and it explains intermolecular interaction. For a multicomponent system,

$$g^C = \sum_i x_i \ln \frac{\Phi_i}{x_i} + 5 \sum_i q_i x_i \, ln \frac{\theta_i}{\Phi_i}$$

$$g^R = -\sum_i q_i x_i \ln \left(\sum_j \theta_j \tau_{ji} \right)$$

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j}, \qquad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j}, \qquad \tau_{ji} = \exp\left[\frac{-\left(u_{ji} - u_{ii}\right)}{RT}\right] \qquad (\tau_{ii} = \tau_{jj} = 1)$$

Equation 3. UNIQUAC equation

Function g^C contains pure-species parameters only, whereas function g^R incorporates two binary parameters for each pair of molecules. In addition, r_i, q_i and u_{ij} reflect the relative molecular volume, relative molecular surface area and influence of temperature, respectively.

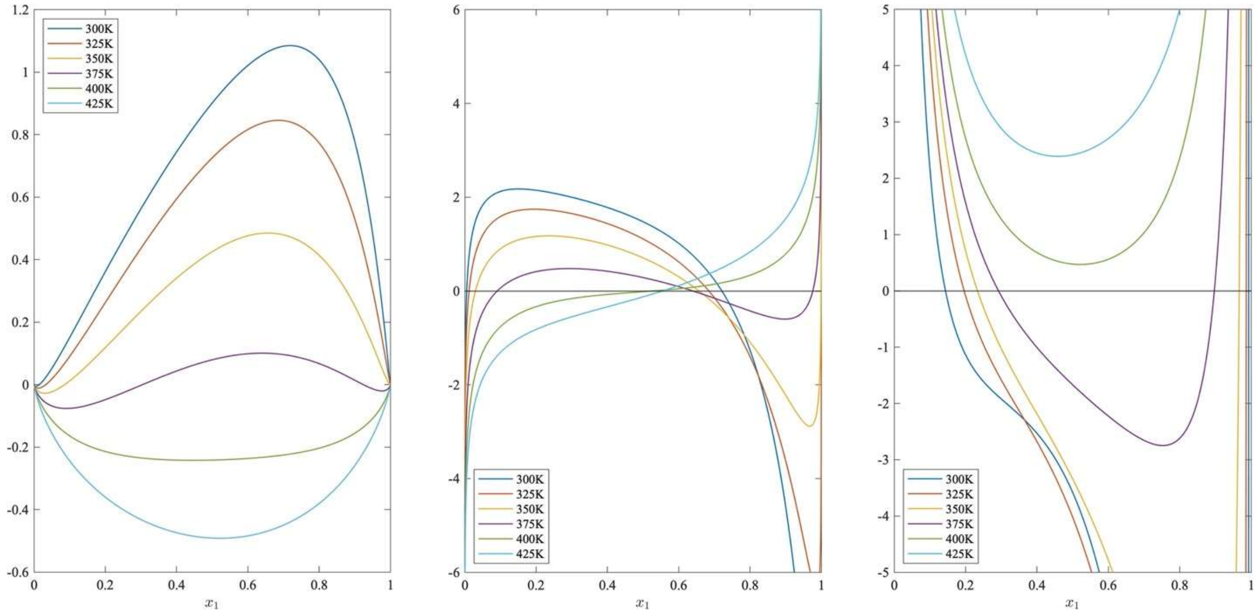
Unlike UNIQUAC, which describes the effects of molecules constituting a mixture in solutions, UNIFAC represents the non-randomness and interaction of solutions in consideration of a specific structural units. These structural units are called *subgroups*. The great advantage of the UNIFAC method is that a relatively small number of subgroups combine to form a very large number of molecules [7, pp. 749–751]. However, UNIQUAC and UNIFAC are not used in this project, since NRTL already gives sufficiently accurate predictions with properly optimized parameters with much less complexity.

2.3 Requirement for LLE: Phase Stability

Criterion of stability for a single-phase binary system is given as [7, p. 438]:

> At fixed temperature and pressure, a single-phase binary mixture is stable if and only if ΔG and its first and second derivatives are continuous functions of x_1, and the second derivative is positive.

In other words, in order for a two-phase equilibrium of a binary system to be stable, it is required that the second derivative is negative, as well as ΔG and its first and second derivatives are continuous functions of x_1.



1a. $\Delta G/RT$ **vs** x_1

1b. $\frac{d(\Delta G/RT)}{dx_1}$ **vs** x_1

1c. $\frac{d^2(\Delta G/RT)}{dx_1^2}$ **vs** x_1

Figure 1. Phase stability profiles at constant T for pentane(1)/sulfolane(2) mixture, by NRTL model

For example, **Figure 1** shows $\Delta G/RT$ and its first and second derivative with respect to x_1 for pentane (1)/sulfolane (2) binary mixture. From the **Figure 1c**, one can interpret approximate temperature range for LLE: isotherms of 300K, 325K, 350K, and 375K have negative value while isotherms of 400K and 425K always have positive values. This implies the LLE is observed for the system at up to certain temperature between 375K and 400K (which is later found to be 390K; see **4.2**).

2.4 NRTL: Parameter Estimation from LLE Data

Parameter estimation for NRTL is essentially about finding a set of optimum τ values from experimental data, since α is conventionally fixed as 0.2, 0.3, etc. depending on the characteristics of the system [9]. Then a proper model function of T can be curve-fitted to the optimum τ values to obtain coefficients in the model function.

Step 1: Set an objective function

Optimum parameters can be found by numerically solving an objective function defined to satisfy equilibrium conditin. Relative isoactivity objective function was used in this project:

$$\mathrm{OF}(\tau_{12}, \tau_{21}) = \sum_i \left(\ln(x_i^\alpha \gamma_i^\alpha) - \ln\left(x_i^\beta \gamma_i^\beta\right)\right)^2$$

$$= \left(\ln(x_1^\alpha \gamma_1^\alpha) - \ln\left(x_1^\beta \gamma_1^\beta\right)\right)^2 + \left(\ln(x_2^\alpha \gamma_2^\alpha) - \ln\left(x_2^\beta \gamma_2^\beta\right)\right)^2$$

Step 2: Find optimum $\boldsymbol{\tau_{12}}$ and $\boldsymbol{\tau_{21}}$

Here, direct search method was used to scan each of τ_{12} and τ_{21} around initially assumed values. Search step must be set low enough to obtain good results, however, too small step size results in slow computing performance.

Step 3: Develop a model function to curve-fit

Once optimum τ values are found, a model function can be developed by inspecting the curve shape or found from literature. In this work, to take account for 1) inverse proportionality, 2) logarithmic component, and 3) linear trend, following model function was developed to be fitted:

$$\tau_{12} = a_{12} + \frac{b_{12}}{T} + c_{12} \ln T + d_{12} T$$

$$\tau_{21} = a_{21} + \frac{b_{21}}{T} + c_{21} \ln T + d_{21} T$$

Step 4: Curve-fit model function to optimum $\boldsymbol{\tau_{12}}$ and $\boldsymbol{\tau_{21}}$

Curve fitting the model function to optimum parameters can be done by computer software packages, such as `lsqcurvefit` function by MATLAB® ‘curve fitting’ Toolbox.

Step 5: Plot LLE diagram with curve-fitted parameters and compare with experimental data

Finally, calculating deviation of NRTL model with fitted parameters from the experimental data is proceeded to examine the accuracy and precision of the model.

2.5 NRTL: Tie-line Calculation Steps

It has been reported by Sørensen et al. [9] that NRTL calculation can be carried out by finding x_1^α and x_1^β at the points where $d(\Delta G)/dx_1 = 0$. However, depending on the profile of $\Delta G - x_1$ curve, this method can result in yielding false solution which then necessitates further maneuver. Therefore, in this work, Tie-line calculation was done by searching optima of both x_1^α and x_1^β from 0 and 1 respectively (or from the values obtained from the previous T) until minimum of an objective function is found. In this work, the search step size is set to be 0.0001 in correspondence to the significant figures of experimental data reported by Ko et al. [10].

Step 1: Set T

Generally, activity coefficient is a function of pressure, temperature, and composition. However, in LLE system, it is a very weak function of pressure since when incompressible-liquid assumption is made. Therefore, in a binary LLE system, the composition of each species in both phases can be determined once T is fixed.

Step 2: Assume x_1^α and x_1^β

It is possible to obtain analytical solution when activity coefficient is represented by simple models. However, it is more viable to numerically solve the set of equations when the model is complicated as in the case of NRTL model used in this work.

By assuming x_1^α and x_1^β, a complete description for the composition of the binary system is obtained since $x_2^\pi = 1 - x_1^\pi$ $(\pi = \alpha, \beta)$. However, it is not the correct description unless LLE criteria are also satisfied:

$$x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta \ (i = 1, 2)$$

Step 3: Set an objective function

To find the composition that satisfy the criteria, an object function is defined as to imply LLE criterion for each species in the equilibrium.

$$\begin{aligned}\mathrm{OF}\left(x_1^\alpha, x_1^\beta\right) &= \sum_i \left(\ln(x_1^\alpha \gamma_1^\alpha) - \ln\left(x_i^\beta \gamma_i^\beta\right)\right)^2 \\ &= \left(\ln(x_1^\alpha \gamma_1^\alpha) - \ln\left(x_1^\beta \gamma_1^\beta\right)\right)^2 + \left(\ln(x_2^\alpha \gamma_2^\alpha) - \ln\left(x_2^\beta \gamma_2^\beta\right)\right)^2\end{aligned}$$

To increase the rate of convergence, the composition information obtained for the previous T can be used as the initial guess.

Step 3: Evaluate objective function with varying x_1^α and x_1^β until optimum is found

The objective function is first calculated with varying initially assumed values of x_1^α and x_1^β until an optimum is found. x_1^α and x_1^β at the optimum are then printed with T that was previously set in **Step 1**. The procedure is repeated again from **Step 1** with $T = T + \Delta T$, until no more LLE is observed either by phase transition or complete miscibility.

3 Results and Discussion

3.1 Optimized NRTL Parameters

Optimal NRTL parameters τ_{12} and τ_{21} for pentane (1)/sulfolane (2) and hexane (1)/sulfolane (2) binary mixtures found in the steps introduced in **3.4** are presented in **Table 1** and **2**.

Table 1. Optimum τ_{12} and τ_{21} with corresponding O.F. value

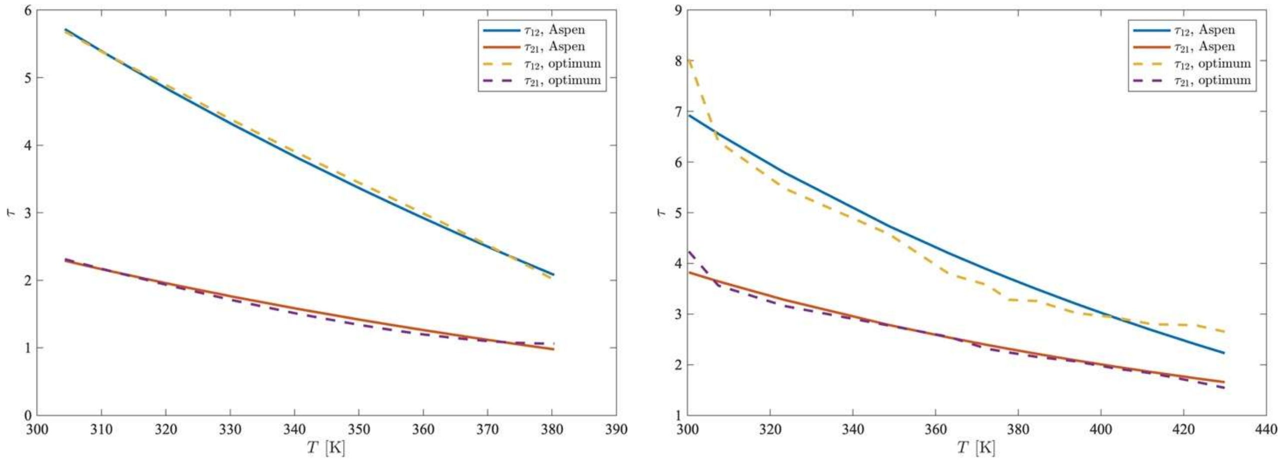
1a. pentane (1)/sulfolane (2) mixture

T/K	τ_{12}	τ_{21}	O.F.
304.31	5.681233	2.310832	0.0000000041
310.80	5.344492	2.150315	0.0000000608
320.72	4.855850	1.918148	0.0000000137
330.41	4.366814	1.703825	0.0000000125
340.50	3.883634	1.502780	0.0000000322
350.15	3.438850	1.337284	0.0000000169
354.82	3.228585	1.267422	0.0000000068
359.64	3.006532	1.202645	0.0000000009
364.75	2.770519	1.145041	0.0000000017
369.78	2.532064	1.101131	0.0000000116
374.11	2.320387	1.075143	0.0000000048
376.49	2.201725	1.066399	0.0000000042
379.39	2.053957	1.061791	0.0000000062
380.35	2.005967	1.060672	0.0000000002

1b. τ_{12} and τ_{21} for hexane (1)/sulfolane (2) mixture

T/K	τ_{12}	τ_{21}	O.F.
300.30	8.031419	4.234521	0.0000000378
307.43	6.408498	3.562131	0.0000000237
323.51	5.477957	3.157205	0.0000000482
348.72	4.578427	2.772902	0.0000000229
363.36	3.786722	2.545974	0.0000000584
372.41	3.574560	2.314090	0.0000000619
377.72	3.282047	2.240975	0.0000000234
384.43	3.256661	2.154913	0.0000000296
393.92	3.020774	2.065671	0.0000000108
403.51	2.931650	1.924569	0.0000000006
412.29	2.799578	1.830223	0.0000000225
422.92	2.778481	1.662621	0.0000000273
429.93	2.651154	1.542555	0.0000000010

NRTL parameters for the system presented by Ko et al. [10] are used as initial guesses for calculation at each temperature. Comparison of the parameters from the literature and from this work are presented in **Figure 2**. The optimum parameters (in **Table 1**) and the curve-fitted model are shown together in **Figure 3**.

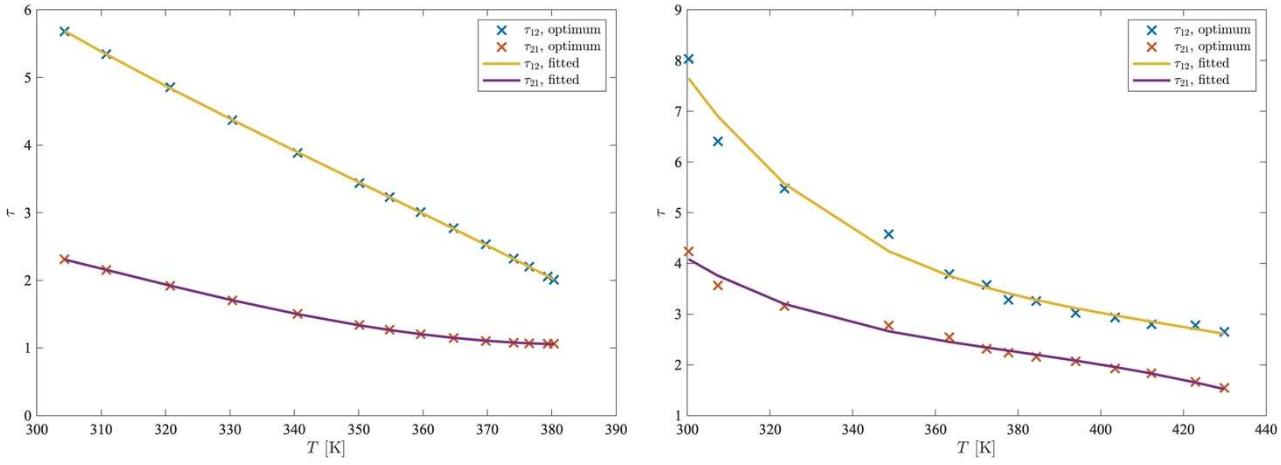


2a. pentane (1)/sulfolane (2) mixture

2b. hexane (1)/sulfolane (2) mixture

Figure 2. τ values found in literature and optimized in this work

As shown in **Figure 2a**, τ_{12} and τ_{21} for pentane (1)/sulfolane (2) mixture calculated in this work (dashed lines) showed more linear and inversely proportional trend with regard to temperature compared to the parameters published in literature (solid lines), respectively [10], [11]. Although optimum parameters for hexane (1)/sulfolane (2) mixture showed irregular and rather undifferentiable curve profile as shown in **Figure 2b**, they showed more inversely proportional trend in general in lower temperature range and more linear or logarithmic trend in higher temperature range.



3a. pentane (1)/sulfolane (2) mixture

3b. hexane (1)/sulfolane (2) mixture

Figure 3. Optimum τ values and curve-fitted models

The curve-fitted parameters for the model function are summarized in **Table 2**. Note that in this work, a new linear term ($d_{12}T$ or $d_{21}T$) is added to the model implemented by Aspen Institute [11] to take account for linear trend.

Table 2. NRTL parameters for calculating τ values

	pentane		hexane	
parameters	**Aspen**	**This work**	**Aspen**	**This work**
α	0.3	0.3	0.3	0.3
a_{12}	16.56	173.431	-20.24	-3322.2729
a_{21}	-21.29	-171.649	-21.29	-2499.5696
b_{12}/K	4095.84	-3696.772	5279.57	115152.3133
b_{21}/K	2842.68	10300.836	3086.87	79997.7140
$c_{12}/(\ln \mathrm{K})^{-1}$	-4.25	-27.215	1.68	552.0269
$c_{21}/(\ln \mathrm{K})^{-1}$	2.49	24.508	2.6	422.1049
d_{12}/K^{-1}	-	-0.422	-	-0.6751
d_{21}/K^{-1}	-	0.629	-	-0.5686

Aspen: $\tau = a + b/T + c\ln T$

This work: $\tau = a + b/T + c\ln T + dT$

3.2 LLE Diagrams by NRTL

With the parameters a, b, c, d that define the function $\tau_{12}(T)$ and $\tau_{21}(T)$ estimated in **4.2**, Now LLE diagram can be plotted by the steps introduced in **3.5**.

3.2.1 Pentane (1)/Sulfolane (2) Binary Mixture

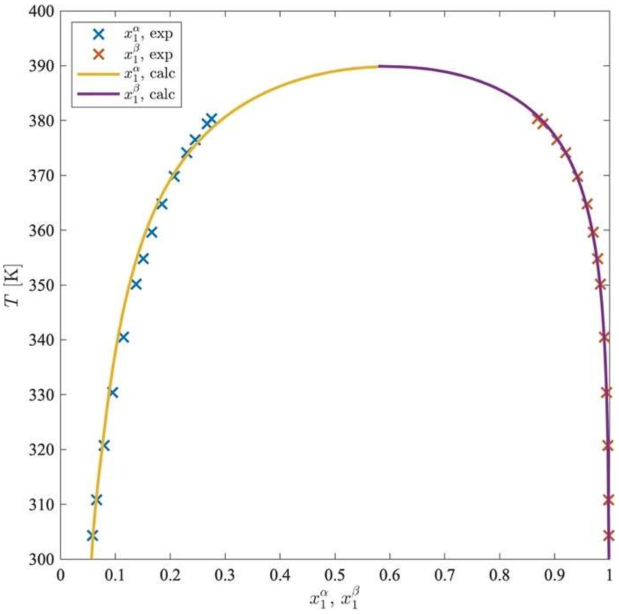


Figure 4. LLE of pentane (1)/sulfolane (2) mixture by NRTL from literature

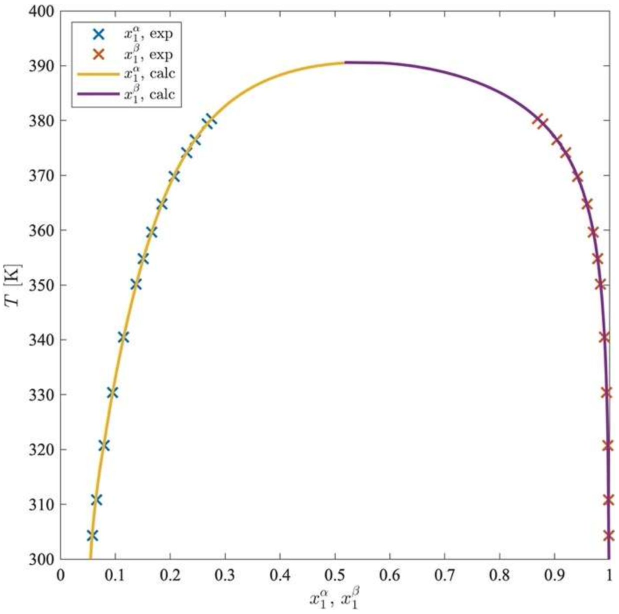


Figure 5. LLE of pentane (1)/sulfolane (2) mixture by NRTL, this work

Figure 4 and **5** present LLE diagram for pentane (1)/sulfolane (2) binary mixture calculated by NRTL model, with τ functions developed by Aspen and optimized in this work, respectively. A quick inspection shows the prediction done by NRTL model correlated in this work is more accurate especially in the sulfolane-rich α phase (yellow solid line). Deviation of the calculation from the experimental data for each temperature are presented in **Table 3**. While the average absolute deviation (AAD) of Aspen NRTL model is 2.6283%, the calculation done in this work resulted in significantly more accurate results with AAD 0.1658%. It is also noteworthy that the maximum deviation observed in Aspen model is 8.5694 for x_1^α at 350.15K, while the maximum deviation observed in this work is 0.5905% for x_1^α at 320.72K. These entries are underlined in **Table 3**. This significant improvement of accuracy is achieved by 1) introduction of a linear term in τ function as well as 2) more accurate curve-fitting.

Table 3. LLE of pentane (1)/sulfolane (2) binary mixture by NRTL, with parameters from literature and this work

	Exp	**NRTL literature**		**NRTL this work**		**Exp**	**NRTL literature**		**NRTL this work**	
T/K	x_1^β	x_1^β	**Err (%)**	x_1^β	**Err (%)**	x_1^α	x_1^α	**Err (%)**	x_1^α	**Err (%)**
304.31	0.9989	0.9989	0.0040	0.9989	0.0010	0.0584	0.0605	3.5274	0.0587	0.5822
310.80	0.9984	0.9984	0.0000	0.9984	0.0000	0.0661	0.0664	0.4841	0.0658	0.4690
320.72	0.9972	0.9971	0.0140	0.9971	0.0050	0.0796	0.0767	3.6181	0.0791	0.5905
330.41	0.9950	0.9947	0.0281	0.9950	0.0020	0.0952	0.0889	6.6702	0.0952	0.0210
340.50	0.9909	0.9903	0.0575	0.9910	0.0121	0.1148	0.1050	8.5366	0.1153	0.4443
350.15	0.9838	0.9827	0.1088	0.9839	0.0122	0.1377	0.1259	8.5694	0.1383	0.4285
354.82	0.9785	0.9771	0.1472	0.9785	0.0020	0.1507	0.1389	7.8235	0.1512	0.3052
359.64	0.9708	0.9691	0.1720	0.9707	0.0103	0.1661	0.1551	6.5984	0.1661	0.0120
364.75	0.9592	0.9574	0.1877	0.9589	0.0344	0.1849	0.1766	4.5051	0.1845	0.2271
369.78	0.9422	0.9409	0.1412	0.9417	0.0488	0.2071	0.2036	1.6659	0.2063	0.3911
374.11	0.9204	0.9205	0.0163	0.9201	0.0282	0.2303	0.2339	1.5632	0.2296	0.3040
376.49	0.9043	0.9058	0.1703	0.9043	0.0022	0.2455	0.2544	3.6293	0.2450	0.1874
379.39	0.8788	0.8830	0.4802	0.8795	0.0751	0.2672	0.2847	6.5344	0.2676	0.1347
380.35	0.8687	0.8739	0.5986	0.8695	0.0944	0.2756	0.2963	7.5181	0.2762	0.2177
			0.1518		**0.0234**			**5.0888**		**0.3082**

NRTL literature AAD (%) : 2.6203
NRTL this work AAD (%) : 0.1658

3.2.2 Hexane (1)/Sulfolane (2) Binary Mixture

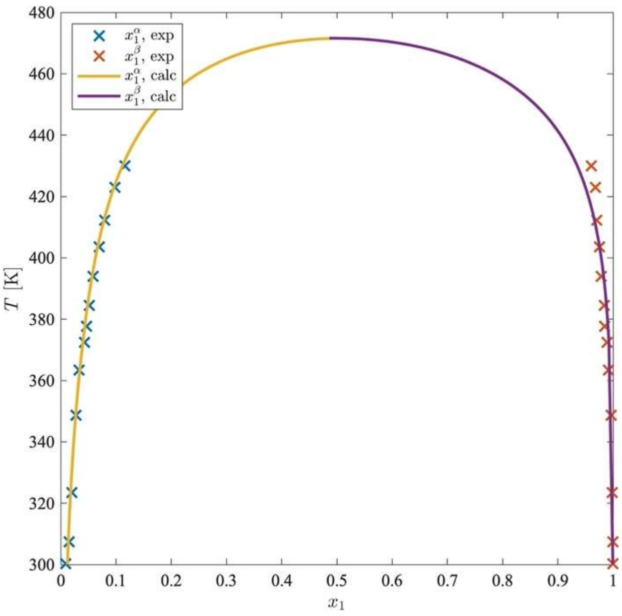


Figure 6. LLE of hexane (1)/sulfolane (2) mixture by NRTL from literature

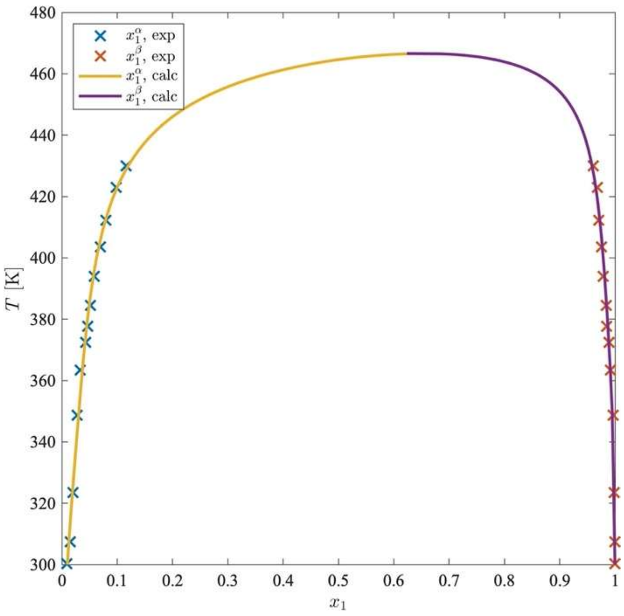


Figure 7. LLE of hexane(1)/sulfolane (2) mixture by NRTL, this work

Figure 6 and **7** present LLE diagram for hexane (1)/sulfolane (2) binary mixture calculated by NRTL model, with τ functions developed by Aspen and optimized in this work, respectively. Similarly to hexane (1)/sulfolane (2) mixture, the prediction done by NRTL model correlated in this work is more accurate especially in the sulfolane-rich α phase (yellow solid line). Deviation of the calculation from the experimental data for each temperature are presented in **Table 4**. While the average absolute deviation (AAD) of Aspen NRTL model is 3.6790%, the calculation done in this work resulted in significantly more accurate results with AAD 2.8920%. It is also noteworthy that the maximum deviation observed in Aspen model is 32.6087 for x_1^α at 300.30K, while the maximum deviation observed in this work is 12.6000% for x_1^α at 370.43K. These entries are underlined in **Table 4**. This significant improvement of accuracy is achieved by 1) introduction of a linear term in τ function as well as 2) more accurate curve-fitting.

Table 4. LLE of hexane (1)/sulfolane (2) binary mixture by NRTL, with parameters from literature and this work

	Exp	NRTL literature		NRTL this work		Exp	NRTL literature		NRTL this work	
T/K	x_1^β	x_1^β	**Err (%)**	x_1^β	**Err (%)**	x_1^α	x_1^α	**Err (%)**	x_1^α	**Err (%)**
300.30	0.9999	0.9997	0.0200	0.9999	0.0050	0.0092	0.0122	32.6087	0.0103	11.5217
307.43	0.9995	0.9996	0.0070	0.9997	0.0190	0.0150	0.0140	6.6000	0.0131	12.6000
323.51	0.9987	0.9991	0.0360	0.9988	0.0120	0.0203	0.0186	8.1281	0.0197	3.1527
348.72	0.9966	0.9971	0.0532	0.9951	0.1535	0.0276	0.0279	1.0507	0.0302	9.3116
363.36	0.9918	0.9948	0.2984	0.9914	0.0393	0.0332	0.0349	5.1205	0.0370	11.3253
372.41	0.9893	0.9925	0.3235	0.9887	0.0586	0.0432	0.0401	7.1065	0.0418	3.3565
377.72	0.9849	0.9908	0.5970	0.9870	0.2142	0.0469	0.0436	7.0362	0.0449	4.2857
384.43	0.9842	0.9881	0.3932	0.9847	0.0508	0.0520	0.0485	6.7115	0.0493	5.0962
393.92	0.9788	0.9829	0.4230	0.9811	0.2380	0.0584	0.0567	2.9281	0.0570	2.4658
403.51	0.9756	0.9756	0.0021	0.9770	0.1404	0.0698	0.0668	4.2550	0.0669	4.0974
412.29	0.9706	0.9663	0.4441	0.9724	0.1824	0.0794	0.0784	1.3098	0.0792	0.2519
422.92	0.9681	0.9501	1.8614	0.9650	0.3181	0.0980	0.0963	1.7143	0.1004	2.4286
429.93	0.9608	0.9352	2.6644	0.9583	0.2571	0.1161	0.1115	3.9621	0.1203	3.6090
			0.5479		**0.1299**			**6.8101**		**5.6540**

NRTL literature AAD (%) : 3.6790
NRTL this work AAD (%) : 2.8920

3.3 Limitations

Although LLE calculations for both mixtures (pentane/sulfolane and hexane/sulfolane) showed great accuracy, some limitations exist for this project:

1) Since two parameters, τ_{12} and τ_{21} have to be optimized, the optimum for objective function was found by a simple search method for both parameters in this project, Although this method has an advantage that local minimum can be avoided, it has a significant limitation that long computing time is required to yield high-precision results. For example, calculating optimum parameters for 13 datapoints for hexane/sulfolane binary system with search range ± 1.5 from initial guess and step size 0.0002 took 713 seconds and 667 seconds for pentane/sulfolane and hexane/sulfolane binary mixture, respectively total. The objective function values were all optimized lower than 10^{-7} in both systems.
2) The focus on this project was on binary mixtures containing an alkane (pentane and hexane) and sulfolane. However, for practical applications, binary LLE predictions offer limited utility compared to ternary or other multi-component mixtures. Nevertheless, this report can serve as a good introduction to understanding principles of LLE using sulfolane as a solvent.

4 Conclusion

Local-composition models for LLE (liquid-liquid equilibrium) were reviewed, and representation of activity coefficient for each component from the excess Gibbs free energy was presented for Wilson equation and NRTL Requirement for LLE in terms of phase stability was given from the Gibbs energy change of mixing and qualitative analysis of Gibbs energy-composition diagram was made.

A new temperature-dependent function for NRTL (non-random-two-liquid) model were developed with an added linear term, and the parameters were fitted to experimental data for two alkane (pentane or hexane)/sulfolane binary mixtures from literature, yielding greatly improved accuracy compared to NRTL model with temperature-dependent function developed by Aspen Institute. LLE tie-lines for the two systems were obtained from 300K to UCST.

The parameter optimization was highly accurate with minimizing the isoactivity objective function as small as 10^{-7}, however, the process took more than 10 minutes for each dataset due to its simple search method. More efficient ways to find the optima can be further studied to perform in the same accuracy with reduced computing time.

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6 Appendix

Appendix A. Calculation of Activity Coefficient from Local-Composition Models

A.1 Wilson Equation

The relation between the activity coefficient and excess Gibbs free energy is shown as below.

$$\ln \gamma_1 = \frac{\bar{G}_1^E}{RT} = \frac{G^E}{RT} + x_2 \frac{d\left(\frac{G^E}{RT}\right)}{dx_1}$$

$$\ln \gamma_2 = \frac{\bar{G}_2^E}{RT} = \frac{G^E}{RT} - x_1 \frac{d\left(\frac{G^E}{RT}\right)}{dx_1}$$

$$\begin{aligned}\frac{G^E}{RT} &= -[x_1 \ln(x_1 + (1 - x_1)\Lambda_{12}) + (1 - x_1) \ln(x_1\Lambda_{21} + 1 - x_1)] \\ &= -[x_1 \ln(x_1(1 - \Lambda_{12}) + \Lambda_{12}) + (1 - x_1)\ln\,(x_1(\Lambda_{21} - 1) + 1)]\end{aligned}$$

$$\frac{d}{dx_1}\left(\frac{G^E}{RT}\right) = -\left[\ln(x_1 + x_2\Lambda_{12}) + \frac{x_1(1 - \Lambda_{12})}{x_1 + x_2\Lambda_{12}} - \ln(x_1\Lambda_{21} + x_2) + \frac{x_2(\Lambda_{21} - 1)}{x_1\Lambda_{21} + x_2}\right]$$

For activity coefficient of species 1,

$$\begin{aligned}\ln \gamma_1 = \frac{G^E}{RT} + x_2 \frac{d\left(\frac{G^E}{RT}\right)}{dx_1} \\ &= -x_1[\ln(x_1 + x_2\Lambda_{12}) + x_2 \ln(x_2 + x_1\Lambda_{21})] \\ &\quad - \left[x_2 \ln(x_1 + x_2\Lambda_{12}) + \frac{x_1x_2(1 - \Lambda_{12})}{x_1 + x_2\Lambda_{12}} - x_2 \ln(x_1\Lambda_{21} + x_2) + \frac{x_2^2(\Lambda_{21} - 1)}{x_1\Lambda_{21} + x_2}\right] \\ &= -\left[\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{x_1(1 - \Lambda_{12})}{x_1 + x_2\Lambda_{12}} + \frac{x_2(\Lambda_{21} - 1)}{x_2 + x_1\Lambda_{21}}\right)\right]\end{aligned}$$

$$\frac{x_1(1-\Lambda_{12})}{x_1+x_2\Lambda_{12}}+\frac{x_2(\Lambda_{21}-1)}{x_2+x_1\Lambda_{21}}=\frac{x_1(1-\Lambda_{12})(x_2+x_1\Lambda_{21})+x_2(\Lambda_{21}-1)(x_1+x_2\Lambda_{12})}{(x_1+x_2\Lambda)(x_2+\mathrm{x}_1\Lambda_{21})}$$

$$=\frac{x_1^2\Lambda_{21}+x_1x_2-x_1^2\Lambda_{12}\Lambda_{21}-x_1x_2\Lambda_{12}+x_1x_2\Lambda_{21}+x_2^2\Lambda_{21}\Lambda_{12}-x_1x_2-x_2^2\Lambda_{12}}{(x_1+x_2\Lambda_{12})(x_2+x_1\Lambda_{21})}$$

$$=\frac{\mathrm{x}_1\Lambda_{21}+(x_2-x_1)\Lambda_{21}\Lambda_{12}-x_2\Lambda_{12}}{(x_1+x_2\Lambda_{12})(x_2+x_1\Lambda_{21})}=\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}-\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}$$

$$\therefore \ln\gamma_1=-\left[\ln(x_1+x_2\Lambda_{12})+x_2\left(\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}-\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}\right)\right]$$

Activity coefficient of species 2 is calculated likewise:

$$\ln\gamma_2=-[x_1\ln(x_1+x_2\Lambda_{12})+x_2\ln(x_2+x_1\Lambda_{21})]$$

$$+\left[x_1\ln(x_1+x_2\Lambda_{12})+\frac{x_1^2(1-\Lambda_{12})}{x_1+x_2\Lambda_{12}}-x_1\ln(x_1\Lambda_{21}+x_2)+\frac{x_1x_2(\Lambda_{21}-1)}{x_1\Lambda_{21}+x_2}\right]$$

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

$$\frac{x_1(1-\Lambda_{12})}{x_1+x_2\Lambda_{12}}+\frac{x_2(\Lambda_{21}-1)}{x_2+x_1\Lambda_{21}}=\frac{x_1(1-\Lambda_{12})(x_2+x_1\Lambda_{21})+x_2(\Lambda_{21}-1)(x_1+x_2\Lambda_{12})}{(x_1+x_2\Lambda_{12})(x_2+x_1\Lambda_{21})}$$

$$=\frac{x_1^2\Lambda_{21}+x_1x_2-x_1^2\Lambda_{12}\Lambda_{21}-x_1x_2\Lambda_{12}+x_1x_2\Lambda_{21}+x_2^2\Lambda_{12}\Lambda_{21}-x_1x_2-x_2^2\Lambda_{12}}{(x_1+x_2\Lambda_{12})(x_2+x_1\Lambda_{21})}$$

$$=\frac{x_1\Lambda_{21}+(x_2^2-x_1^2)\Lambda_{12}\Lambda_{21}-x_2\Lambda_{12}}{(x_1+x_2\Lambda_{12})(x_2+x_1\Lambda_{21})}=\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}-\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}$$

$$\therefore \ln\gamma_2=-\left[\ln(x_2+x_1\Lambda_{21})+x_1\left(\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}-\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}\right)\right]$$

For infinite dilution (x_1→0 or x_2→0), these equations become :

$$\lim_{\substack{x_1\to 0\\(x_2\to 1)}}\ln\gamma_1=\ln\gamma_1^{\infty}=-\ln\Lambda_{12}+1-\Lambda_{21}$$

$$\lim_{\substack{x_2\to 0\\(x_1\to 1)}}\ln\gamma_2=\ln\gamma_2^{\infty}=-\ln\Lambda_{21}+1-\Lambda_{12}$$

A.2 NRTL

Using NRTL, the relation between the activity coefficient and excess Gibbs free energy is expressed as follows.

$$\frac{G^E}{RT} = x_1x_2\left(\frac{G_{21}\tau_{21}}{x_1 + x_2G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1G_{12}}\right) = \frac{G_{21}\tau_{21}x_1x_2}{x_1 + x_2G_{21}} + \frac{G_{12}\tau_{12}x_1x_2}{x_2 + x_1G_{12}}$$

$$\begin{aligned}\frac{d}{dx_1}\left(\frac{G^E}{RT}\right) &= \frac{(x_2 - x_1)(x_1+x_2G_{21})G_{21}\tau_{21} - (1 - G_{21})G_{21}\tau_{21}x_1x_2}{(x_1 + x_2G_{21})^2} \\ &+ \frac{(x_2 - x_1)(x_2 + x_1G_{12})G_{12}\tau_{12} - (G_{12} - 1)G_{12}\tau_{12}x_1x_2}{(x_2 + x_1G_{12})^2} \\ &= \frac{G_{21}\tau_{21}x_1x_2 + G_{21}^2\tau_{21}x_2^2 - G_{21}\tau_{21}x_1^2 - G_{21}^2\tau_{21}x_1x_2 - G_{21}\tau_{21}x_1x_2 + G_{21}^2\tau_{21}x_1x_2}{(x_1 + x_2G_{21})^2} \\ &+ \frac{G_{12}\tau_{12}x_2^2 + G_{12}^2\tau_{12}x_1x_2 - G_{12}\tau_{12}x_1x_2 - G_{12}^2\tau_{12}x_1^2 - G_{12}^2\tau_{12}x_1x_2 + G_{12}\tau_{12}x_1x_2}{(x_2 + x_1G_{12})^2}\end{aligned}$$

$$\therefore \frac{d}{dx_1}\left(\frac{G^E}{RT}\right) = \frac{G_{21}^2\tau_{21}x_2^2 - G_{21}\tau_{21}x_1^2}{(x_1 + x_2G_{21})^2} + \frac{G_{12}\tau_{12}x_2^2 - G_{12}^2\tau_{12}x_1^2}{(x_2 + x_1G_{12})^2}$$

$$\begin{aligned}\ln\gamma_1 &= \frac{G^E}{RT} + x_2\frac{d\left(\frac{G^E}{RT}\right)}{dx_1} \\ &= \frac{G_{21}\tau_{21}x_1x_2}{x_1 + x_2G_{21}} + \frac{G_{12}\tau_{12}x_1x_2}{x_2 + x_1G_{12}} + \frac{G_{21}^2\tau_{21}x_2^3 - G_{21}\tau_{21}x_1^2x_2}{(x_1 + x_2G_{21})^2} + \frac{G_{12}\tau_{12}x_2^3 - G_{12}^2\tau_{12}x_1^2x_2}{(x_2 + x_1G_{12})^2} \\ &= \frac{G_{21}\tau_{21}x_1x_2(x_1 + x_2G_{21}) + G_{21}^2\tau_{21}x_2^3 - G_{21}\tau_{21}x_1^2x_2}{(x_1 + x_2G_{21})^2} \\ &+ \frac{G_{12}\tau_{12}x_1x_2(x_2 + x_1G_{12}) + G_{12}\tau_{12}x_2^3 - G_{12}^2\tau_{12}x_1^2x_2}{(x_2 + x_1G_{12})^2} \\ &= \frac{G_{21}\tau_{21}x_1^2x_2 + G_{21}^2\tau_{21}x_1x_2^2 + G_{21}^2\tau_{21}x_2^3 - G_{21}\tau_{21}x_1^2x_2}{(x_1 + x_2G_{21})^2} \\ &+ \frac{G_{12}\tau_{12}x_1x_2^2 + G_{12}^2\tau_{12}x_1^2x_2 + G_{12}\tau_{12}x_2^3 - G_{12}^2\tau_{12}x_1^2x_2}{(x_2 + x_1G_{12})^2} \\ &= \frac{x_2^2G_{21}^2\tau_{21}}{(x_1 + x_2G_{21})^2} + \frac{x_2^2G_{12}\tau_{12}}{(x_2 + x_1G_{12})^2}\end{aligned}$$

$$\therefore \ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}} \right]$$

Likewise,

$$\begin{aligned}
\ln \gamma_2 &= \frac{G_{21}\tau_{21}x_1x_2}{x_1 + x_2G_{21}} + \frac{G_{12}\tau_{12}x_1x_2}{x_2 + x_1G_{12}} - \frac{G_{21}^2\tau_{21}x_1x_2^2 - G_{21}\tau_{21}x_1^3}{(x_1 + x_2G_{21})^2} - \frac{G_{12}\tau_{12}x_1x_2^2 - G_{12}^2\tau_{12}x_1^3}{(x_2 + x_1G_{12})^2} \\
&= \frac{G_{21}\tau_{21}x_1^2x_2 + G_{21}^2\tau_{21}x_1x_2^2 - G_{21}^2\tau_{21}x_1x_2^2 + G_{21}\tau_{21}x_1^3}{(x_1 + x_2G_{21})^2} \\
&+ \frac{G_{12}\tau_{12}x_1x_2^2 + G_{12}^2\tau_{12}x_1^2x_2 - G_{12}\tau_{12}x_1x_2^2 + G_{12}^2\tau_{12}x_1^3}{(x_2 + x_1G_{12})^2} \\
&= \frac{x_1^2G_{21}\tau_{21}}{(x_1 + x_2G_{21})^2} + \frac{x_1^2G_{12}^2\tau_{12}}{(x_2 + x_1G_{12})^2}
\end{aligned}$$

$$\therefore \ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{!2}}{x_2 + x_{!}G_{12}} \right)^2 + \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} \right]$$

The infinite-dilution(x$_1$→0 or x$_2$→0) values of the activity coefficients are given by equations :

$$\lim_{\substack{x_1 \to 0 \\ (x_2 \to 1)}} \ln \gamma_1 = \ln \gamma_1^\infty = \tau_{21} + \tau_{12}G_{12} = \tau_{21} + \tau_{12}\exp\left(-\alpha\tau_{12}\right)$$

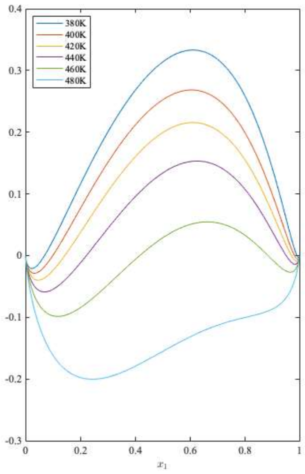
$$\lim_{\substack{x_2 \to 0 \\ (x_1 \to 1)}} \ln \gamma_2 = \ln \gamma_2^\infty = \tau_{12} + \tau_{21}G_{21} = \tau_{12} + \tau_{21}\exp\left(-\alpha\tau_{21}\right)$$

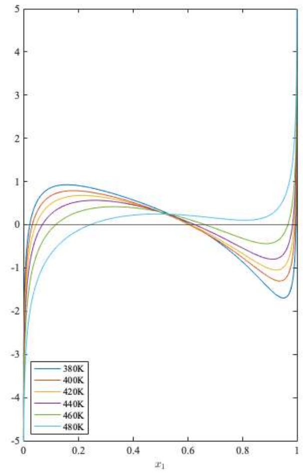
Appendix B. MATLAB® Codes with Execution Results

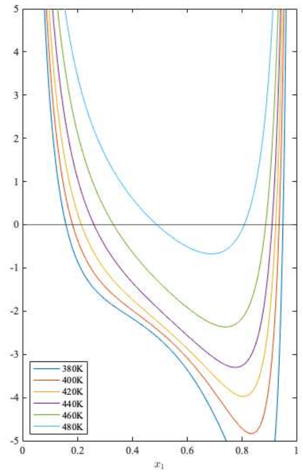
B.1 Gibbs Energy Diagram (‘Gx_plot.m’)

```
clear all
close all
clc

% alkane = 'pentane'; T_range = [300 325 350 375 400 425];
alkane = 'hexane';  T_range = [380 400 420 440 460 480];

load([alkane '_expdata.mat'])
load([alkane '_parameters'])
load([alkane '_parameters_opt.mat'])

parameters = parameters_Aspen;
parameters = parameters_opt;


set(groot,'defaultLineMarkerSize', 10, ...
    'defaultLineLineWidth', 1, ...
    'defaultAxesFontName', 'Times', ...
    'defaultAxesFontSize', 12);

expT = data(:,1);
expX11 = data(:,2);
expX12 = data(:,3);

Gxplot = figure('Position',[0 0 400 600]);
dGxplot = figure('Position',[400 0 400 600]);
ddGxplot = figure('Position',[800 0 400 600]);

figure(2),plot(linspace(0,1,1001),0,'-k');
m = 100000;
stop = 0;
for j = 1:6
    if stop == 1
        break
    end
    T = T_range(j);

    for i = 1:m+1
        x1(i) = (i-1)/m;
        deltaGRT(i) = G_NRTL(parameters, T,x1(i));
    end

    for i = 1:m
        d_deltaGRT(i) = ( deltaGRT(i+1) - deltaGRT(i) ) / (1/m);
    end

    for i = 1:m-1
        dd_deltaGRT(i) = ( d_deltaGRT(i+1) - d_deltaGRT(i) ) / (1/m);
    end

    figure(1),plot(x1,deltaGRT,'DisplayName',[num2str(T) 'K']); hold on
    xlim([0 1]);
    figure(2),plot(x1(1:m),d_deltaGRT,'DisplayName',[num2str(T) 'K']); hold on
    xlim([0 1]); ylim([-5 5])
    figure(3),plot(x1(1:m-1),dd_deltaGRT,'DisplayName',[num2str(T) 'K']); hold on
    xlim([0 1]); ylim([-5 5])

end

figure(1),legend('Location','northwest','AutoUpdate','off')
xlabel('$$x_1$$','Interpreter','latex')
exportgraphics(gca,[alkane '_G.jpg'],'Resolution',300)
```

```
figure(2),legend('Location','southwest','AutoUpdate','off')
yline(0,'LineWidth',1)
xlabel('$$x_1$$','Interpreter','latex')
exportgraphics(gca,[alkane '_dG.jpg'],'Resolution',300)

figure(3),legend('Location','southwest','AutoUpdate','off')
yline(0,'LineWidth',1)
xlabel('$$x_1$$','Interpreter','latex')
exportgraphics(gca,[alkane '_ddG.jpg'],'Resolution',300)

function delta_GRT = G_NRTL(parameters, T,x1)

alpha = 0.3;
a12 = parameters(1);
b12 = parameters(2);
c12 = parameters(3);
d12 = parameters(4);
a21 = parameters(5);
b21 = parameters(6);
c21 = parameters(7);
d21 = parameters(8);

tau12 = a12 + b12/T + c12*log(T) + d12*T;
tau21 = a21 + b21/T + c21*log(T) + d21*T;
G12 = exp(-alpha*tau12);
G21 = exp(-alpha*tau21);

x2 = 1 - x1;
delta_GRT = ( x1*log(x1) + x2*log(x2) ...
    + x1*x2*( (G21*tau21)/(x1+x2*G21) + (G12*tau12)/(x2+x1*G12) ));

end
```







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B.2 NRTL Parameter Optimization ('find_tau.m')

```
clear all
close all
% clc

% alkane = 'pentane'; lb = 0; ub = 6;
alkane = 'hexane';  lb = 1; ub = 9;

fprintf(['\n\n << FOR ' upper(alkane) ' >>\n'])
load([alkane '_expdata.mat'])
load([alkane '_parameters'])

a12 = parameters_Aspen(1);
b12 = parameters_Aspen(2);
c12 = parameters_Aspen(3);
a21 = parameters_Aspen(5);
b21 = parameters_Aspen(6);
c21 = parameters_Aspen(7);

tau12_Aspen = a12 + b12./data(:,1) + c12.*log(data(:,1));
tau21_Aspen = a21 + b21./data(:,1) + c21.*log(data(:,1));

set(groot,'defaultLineMarkerSize', 10, ...
    'defaultLineLineWidth', 2, ...
    'defaultAxesFontName', 'Times', ...
    'defaultAxesFontSize', 12, ...
    'defaultLegendFontSize', 12);

expT = data(:,1);
expX11 = data(:,2);
expX12 = data(:,3);
clear data

m = 5000;    % Adjust precision of finding optimal tau
range = 3;
% fprintf(' m = %d\n',m)
fprintf('==========================================\n')
fprintf('  T/K      tau12     tau21        OF\n')
fprintf('------------------------------------------\n')

tic
for k = 1 : size(expT)

    T = expT(k);
    x11 = expX11(k);
    x12 = expX12(k);

    [tau12_opt(k), tau21_opt(k), OF(k)] = opt_tau(tau12_Aspen(k), tau21_Aspen(k), x11,
x12, m, range);

    fprintf(' %.2f  %f  %f  %.10f\n', ...
        T, tau12_opt(k), tau21_opt(k), OF(k))
end

fprintf('------------------------------------------\n')
toc

tau12_opt = tau12_opt';
tau21_opt = tau21_opt';

fig = figure('Position',[0 10000 600 400]);
plot(expT,tau12_Aspen,'DisplayName','$\tau_{12}$, ${\mathrm {Aspen}}$'); hold on
plot(expT,tau21_Aspen,'DisplayName','$\tau_{21}$, ${\mathrm {Aspen}}$');
plot(expT,tau12_opt,'--','DisplayName','$\tau_{12}$, ${\mathrm {optimum}}$');
plot(expT,tau21_opt,'--','DisplayName','$\tau_{21}$, ${\mathrm {optimum}}$');
xlabel('$$T$$ $${\mathrm {[K]}}$$','Interpreter','latex')
```

```
ylabel('$$\tau$$', 'Interpreter','latex')
% xlim([300 390])
ylim([lb ub])
legend('Interpreter','latex')

exportgraphics(gca,[alkane '_tau_comparison.jpg'],'Resolution',300)

T_data = expT;
tau12_data = tau12_opt;
tau21_data = tau21_opt;
clear expT tau12_opt tau21_opt

opts = optimset('Display','off');
fun = @(k,xdata) k(1) + k(2)./xdata + k(3).*log(xdata) +k(4)*xdata ;

k12_0 = [6,1,0,-1];
k21_0 = [2,1,0,-1];

k12 = lsqcurvefit(fun, k12_0, T_data, tau12_data,[],[],opts);
k21 = lsqcurvefit(fun, k21_0, T_data, tau21_data,[],[],opts);
fprintf('\n')
fprintf(' Fitted coefficients:\n\n')
fprintf(' a12 %11.4f    ', k12(1))
fprintf(' a21 %11.4f\n', k21(1))
fprintf(' b12 %11.4f    ', k12(2))
fprintf(' b21 %11.4f\n', k21(2))
fprintf(' c12 %11.4f    ', k12(3))
fprintf(' c21 %11.4f\n', k21(3))
fprintf(' d12 %11.4f    ', k12(4))
fprintf(' d21 %11.4f\n', k21(4))

parameters_opt = [k12, k21];
save([alkane '_parameters_opt.mat'], 'parameters_opt')

tau12_fitted = fun(k12,T_data);
tau21_fitted = fun(k21,T_data);

fig = figure('Position',[0 0 600 400]);
plot(T_data,tau12_data,'x'); hold on
plot(T_data,tau21_data,'x');
plot(T_data,tau12_fitted,'-');
plot(T_data,tau21_fitted,'-');
legend(...
    '$$\tau_{12}$$, $\mathrm{optimum}$', ...
    '$$\tau_{21}$$, $\mathrm{optimum}$', ...
    '$$\tau_{12}$$, $\mathrm{fitted}$', ...
    '$$\tau_{21}$$, $\mathrm{fitted}$', ...
    'Interpreter', 'latex','Location','northeast')
xlabel('$$T$$ $${\mathrm {[K]}}$$','Interpreter','latex')
ylabel('$$\tau$$', 'Interpreter','latex')
% xlim([300 390])
ylim([lb ub])
exportgraphics(gca,[alkane '_tau_fitted.jpg'],'Resolution',300)

function [tau12_opt, tau21_opt, OF] = opt_tau(tau12_in, tau21_in, x1alpha, x1beta, m,
range)

    alpha = 0.3;

    for i = 1: m
        tau12 = tau12_in + range * (-0.5 + i/m);

        for j = 1: m
            tau21 = tau21_in + range * (-0.5 + j/m);

            G12 = exp(-alpha*tau12);
            G21 = exp(-alpha*tau21);
```

```
            x1 = x1alpha;
            x2 = 1 - x1;
            gamma12 = exp( x2^2 * ( tau21*( G21/(x1+x2*G21) )^2 + G12*tau12 /
(x2+x1*G12)^2 ) );
            gamma22 = exp( x1^2 * ( tau12*( G12/(x2+x1*G12) )^2 + G21*tau21 /
(x1+x2*G21)^2 ) );

            k11 = x1*gamma12;
            k21 = x2*gamma22;

            x1 = x1beta;
            x2 = 1 - x1;
            gamma11 = exp( x2^2 * ( tau21*( G21/(x1+x2*G21) )^2 + G12*tau12 /
(x2+x1*G12)^2 ) );
            gamma21 = exp( x1^2 * ( tau12*( G12/(x2+x1*G12) )^2 + G21*tau21 /
(x1+x2*G21)^2 ) );

            k12 = x1*gamma11;
            k22 = x2*gamma21;

            OF(i,j) = (k11 - k12)^2 + (k21 - k22)^2;

        end
    end

    [minOF1, index1] = min(OF);
    [minOF2, index2] = min(minOF1);
    ind1 = index1(index2);
    ind2 = index2;
    OF = minOF2;
    tau12_opt = tau12_in + range * (-0.5 + ind1/m);
    tau21_opt = tau21_in + range * (-0.5 + ind2/m);
end
```

```
 << FOR HEXANE >>
==========================================
  T/K      tau12      tau21         OF
------------------------------------------
 300.30  8.031419  4.234521  0.0000000378
 307.43  6.408498  3.562131  0.0000000237
 323.51  5.477957  3.157205  0.0000000482
 348.72  4.578427  2.772902  0.0000000227
 363.36  3.786722  2.545974  0.0000000564
 372.41  3.574560  2.314090  0.0000000619
 377.72  3.282047  2.240975  0.0000000234
 384.43  3.256661  2.154913  0.0000000296
 393.92  3.020774  2.065671  0.0000000108
 403.51  2.931650  1.924569  0.0000000006
 412.29  2.799578  1.830223  0.0000000225
 422.92  2.778481  1.662621  0.0000000273
 429.93  2.651154  1.542555  0.0000000010
------------------------------------------
Elapsed time is 659.200407 seconds.

 Fitted coefficients:

 a12  -3322.2729     a21  -2499.5696
 b12 115152.3133     b21  79997.7140
 c12     552.0269     c21    422.1049
 d12      -0.6751     d21     -0.5686
```

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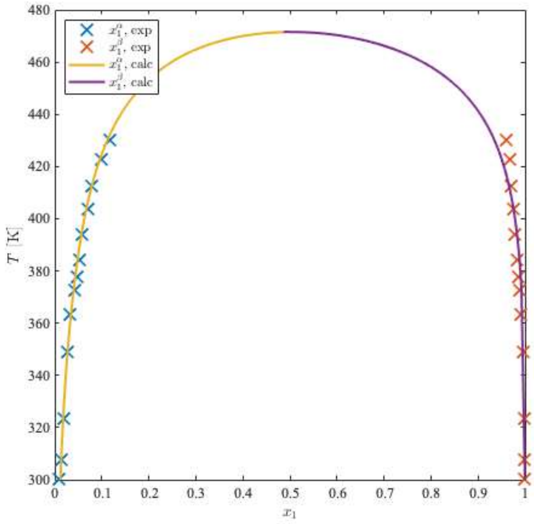
B.3 NRTL LLE Calculation (‘LLE_NRTL.m’)

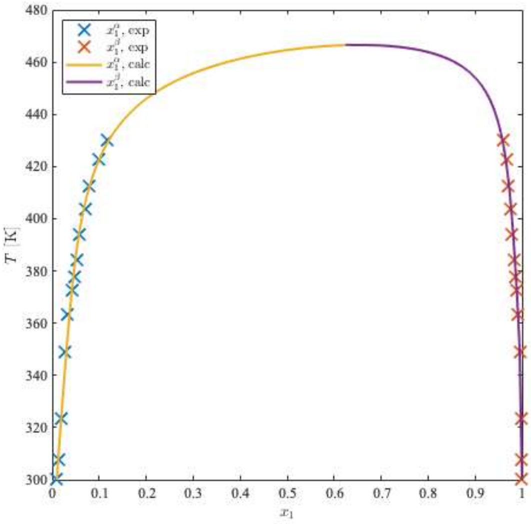
Contents

Full LLE Diagram

```
clear all
close all
clc

% alkane = 'pentane'; Tlb = 300;  Tub = 400;
alkane = 'hexane';  Tlb = 300;  Tub = 480;

load([alkane '_expdata.mat'])
load([alkane '_tau_Aspen.mat'])
load([alkane '_parameters'])
load([alkane '_parameters_opt.mat'])

set(groot,'defaultLineMarkerSize', 10, ...
    'defaultLineLineWidth', 2, ...
    'defaultAxesFontName', 'Times New Roman', ...
    'defaultAxesFontSize', 12);

T_data = data(:,1);
x11_data = data(:,2);
x12_data = data(:,3);


tic

for par = 1:2
clear result
    fprintf('\n\n')
    if par ==1
        parameters = parameters_Aspen;
        fprintf(' Parameters from Aspen')
    else
        parameters = parameters_opt;
        fprintf(' Parameters optimized')
    end

fprintf('\n')
fprintf('=======================\n')
fprintf('  T/K     x11     x12\n')
fprintf('-----------------------\n')
x12_in = 0;
x11_in = 1;
for k = 1:2000

    T = 300 + 0.1*(k-1) ;
    result(k,1) = T;
    fprintf(' %.1f ', T)
    [result(k,3), result(k,2), ~, ~, ~] = NRTL(x12_in, x11_in, parameters, T);

    if result(k,3) >= result(k,2)
        fprintf(' NO LLE!\n')
        result(k,:) = [];
        k = k-1;
        break
    end

    fprintf(' %0.4f  %0.4f\n', result(k,2), result(k,3))
    x12_in = result(k,3);
    x11_in = result(k,2);
```

```
end
fprintf('\n')
toc

LLE = figure('Position',[0 0 500 500]);

plot(x12_data, T_data, 'x'); hold on
plot(x11_data, T_data, 'x');
plot(result(:,3), result(:,1), '-');
plot(result(:,2), result(:,1), '-');
pbaspect([1 1 1])
xlim([0 1])
ylim([Tlb Tub])
legend(...
    '$$x_1^\alpha$$, $${\mathrm {exp}}$$', ...
    '$$x_1^\beta$$, $${\mathrm {exp}}$$', ...
    '$$x_1^\alpha$$, $${\mathrm {calc}}$$', ...
    '$$x_1^\beta$$, $${\mathrm {calc}}$$ ', ...
    'Interpreter','latex', ...
    'Location','northwest')
xlabel('$$x_1$$','Interpreter','latex')
ylabel('$$T$$ $${\mathrm {[K]}}$$','Interpreter','latex')
exportgraphics(gca,[alkane '_LLE_' num2str(par) '.jpg'],'Resolution',300)
end
```





NRTL Result for Error Analysis

```
clear all
close all
% clc

% alkane = 'pentane'; Tlb = 300;  Tub = 400;
alkane = 'hexane';  Tlb = 300;  Tub = 480;

load([alkane '_expdata.mat'])
load([alkane '_tau_Aspen.mat'])
load([alkane '_parameters'])
load([alkane '_parameters_opt.mat'])

set(groot,'defaultLineMarkerSize', 10, ...
    'defaultLineLineWidth', 2, ...
    'defaultAxesFontName', 'Times New Roman', ...
    'defaultAxesFontSize', 12);
```

```
T_data = data(:,1);
x11_data = data(:,2);
x12_data = data(:,3);

for par = 1:2
    fprintf('\n\n')
    if par ==1
        parameters = parameters_Aspen;
        fprintf([' < ' upper(alkane) '/SULFOLANE > w/ parameters from literature'])
    else
        parameters = parameters_opt;
        fprintf([' < ' upper(alkane) '/SULFOLANE > w/ parameters optimized'])
    end
    fprintf('\n')
    fprintf('============================================================\n')
    fprintf('           Exp     NRTL              Exp     NRTL\n')
    fprintf(' T/K       x11     x11     err(%%)    x12     x12     err(%%)\n')
    fprintf('------------------------------------------------------------\n')

    x12_in = 0;
    x11_in = 1;
    tic

    for k = 1:size(T_data)

        T = T_data(k);
        result(k,1) = T;

        [result(k,3), result(k,2), tau12(k), tau21(k), OF(k)] = NRTL(x12_in, x11_in,
parameters, T);
        err(k,1) = abs( ( result(k,2) - data(k,2) ) / data(k,2) ) *100 ; % x11 error
        err(k,2) = abs( ( result(k,3) - data(k,3) ) / data(k,3) ) *100 ; % x12 error
        x12_in = result(k,3);
        x11_in = result(k,2);
        fprintf(' %.2f    %.4f  %.4f  %.4f    %.4f  %.4f  %0.4f\n', ...
            T, x11_data(k), result(k,2), err(k,1), x12_data(k), result(k,3), err(k,2))

    end
    fprintf('------------------------------------------------------------\n')

    time = toc;
    meanerr(1) = mean(err(:,1));
    meanerr(2) = mean(err(:,2));
    toterr = mean(meanerr);

    fprintf('     x11 error %7.4f\n', meanerr(1))
    fprintf('     x12 error %7.4f\n', meanerr(2))
    fprintf(' overall error %7.4f\n', toterr)
    fprintf('  elapsed time %7.4f seconds\n', time)



end
```

```
< HEXANE/SULFOLANE > w/ parameters from literature
============================================================
           Exp     NRTL              Exp     NRTL
 T/K       x11     x11     err(%)    x12     x12     err(%)
------------------------------------------------------------
 300.30    0.9999  0.9997  0.0200    0.0092  0.0122  32.6087
 307.43    0.9995  0.9996  0.0070    0.0150  0.0140  6.6000
 323.51    0.9987  0.9991  0.0360    0.0203  0.0186  8.1281
 348.72    0.9966  0.9971  0.0532    0.0276  0.0279  1.0507
 363.36    0.9918  0.9948  0.2984    0.0332  0.0349  5.1205
 372.41    0.9893  0.9925  0.3235    0.0432  0.0401  7.1065
 377.72    0.9849  0.9908  0.5970    0.0469  0.0436  7.0362
```

```
 384.43    0.9842  0.9881  0.3932    0.0520  0.0485  6.7115
 393.92    0.9788  0.9829  0.4230    0.0584  0.0567  2.9281
 403.51    0.9756  0.9756  0.0021    0.0698  0.0668  4.2550
 412.29    0.9706  0.9663  0.4441    0.0794  0.0784  1.3098
 422.92    0.9681  0.9501  1.8614    0.0980  0.0963  1.7143
 429.93    0.9608  0.9352  2.6644    0.1161  0.1115  3.9621
------------------------------------------------------------
     x11 error  0.5479
     x12 error  6.8101
 overall error  3.6790
  elapsed time  3.7119 seconds


 < HEXANE/SULFOLANE > w/ parameters optimized
============================================================
           Exp     NRTL                Exp     NRTL
 T/K       x11     x11     err(%)      x12     x12     err(%)
------------------------------------------------------------
 300.30    0.9999  0.9999  0.0050    0.0092  0.0103  11.5217
 307.43    0.9995  0.9997  0.0190    0.0150  0.0131  12.6000
 323.51    0.9987  0.9988  0.0120    0.0203  0.0197  3.1527
 348.72    0.9966  0.9951  0.1535    0.0276  0.0302  9.3116
 363.36    0.9918  0.9914  0.0393    0.0332  0.0370  11.3253
 372.41    0.9893  0.9887  0.0586    0.0432  0.0418  3.3565
 377.72    0.9849  0.9870  0.2142    0.0469  0.0449  4.2857
 384.43    0.9842  0.9847  0.0508    0.0520  0.0493  5.0962
 393.92    0.9788  0.9811  0.2380    0.0584  0.0570  2.4658
 403.51    0.9756  0.9770  0.1404    0.0698  0.0669  4.0974
 412.29    0.9706  0.9724  0.1824    0.0794  0.0792  0.2519
 422.92    0.9681  0.9650  0.3181    0.0980  0.1004  2.4286
 429.93    0.9608  0.9583  0.2571    0.1161  0.1203  3.6090
------------------------------------------------------------
     x11 error  0.1299
     x12 error  5.6540
 overall error  2.8920
  elapsed time  2.1997 seconds
```

Function

```
function [x12_cal, x11_cal, tau12, tau21, minOF2] = NRTL(x12_in,x11_in,parameters, T)

alpha = 0.3;
a12 = parameters(1);
b12 = parameters(2);
c12 = parameters(3);
d12 = parameters(4);
a21 = parameters(5);
b21 = parameters(6);
c21 = parameters(7);
d21 = parameters(8);

tau12 = a12 + b12/T + c12*log(T) + d12*T;
tau21 = a21 + b21/T + c21*log(T) + d21*T;
G12 = exp(-alpha*tau12);
G21 = exp(-alpha*tau21);

n = 10*10^4;
x12 = zeros(n,1);
x11 = zeros(n,1);
% OF = zeros(n/2);
stop_i = 0;
stop_j = 0;

for i = 1:n
    x12(i) = x12_in + (i-1)/n;

    for j = 1:n
```

```
        if stop_j ==1
            stop_j = 0;
            break
        end
        x11(j) = x11_in - (j-1)/n;

        % alpha phase (rich in 2)
        x1 = x12(i);
        x2 = 1 - x1;
        gamma11 = exp( x2^2 * ( tau21*( G21/(x1+x2*G21) )^2 + G12*tau12 /
(x2+x1*G12)^2 ) );
        gamma21 = exp( x1^2 * ( tau12*( G12/(x2+x1*G12) )^2 + G21*tau21 /
(x1+x2*G21)^2 ) );

        k11 = x1*gamma11;
        k21 = x2*gamma21;

        % beta phase (rich in 1)
        x1 = x11(j);
        x2 = 1 - x1;
        gamma12 = exp( x2^2 * ( tau21*( G21/(x1+x2*G21) )^2 + G12*tau12 /
(x2+x1*G12)^2 ) );
        gamma22 = exp( x1^2 * ( tau12*( G12/(x2+x1*G12) )^2 + G21*tau21 /
(x1+x2*G21)^2 ) );

        k12 = x1*gamma12;
        k22 = x2*gamma22;

        OF(i,j) = (k11 - k12)^2 + (k21 - k22)^2;

        if j>2
            if OF(i,j) > OF(i,j-1)
                minOF(i) = OF(i,j-1);
                min_j = j-1;
                stop_j = 1;
            end
        end
    end
%     fprintf('\n%f', min(OF(i)));

    if i> 2
        if minOF(i) > minOF(i-1)
            min = minOF(i-1);
            min_i = i-1;
            stop_i = 1;
        end
    end

    if stop_i == 1
        break
    end
end

minOF2 =  min;
x11_cal = x11(min_j);
x12_cal = x12(min_i);

end
```

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