A Web Tool for Generating Ternary LLE Data

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10th April 2008

Abstract

The primary aim of this project was to produce a JavaScript program to estimate Margules constants, generate ternary liquid – liquid equilibria data and plot triangular diagrams.

Overall, this project has produced a useful program for generating ternary diagrams that can be used as a general rule of thumb. Whilst the generated diagrams should not be used for detailed design of extraction processes, they are effective in demonstrating liquid – liquid phase behaviour.

Contents

1 Introduction **3**

2 The Margules Equation **5**
2.1 For Binary System 6
2.2 For Ternary System 6
2.3 Temperature Dependance 7

3 Collecting Binary Data **8**
3.1 Solubilities 8
3.2 Azeotropes 9

4 Program Overview **10**
4.1 Versions of the Program 10
4.1.1 Basic Version 10
4.1.2 Enhanced Version 11
4.2 Structure of Program 11
4.2.1 Directory of files 14
4.2.2 Description of `ternary.js` 15
4.3 Calculation of Binary Constants 15

5 Review of Program's Accuracy **16**
5.1 Type I System:
Water – Toluene – Methanol 16
5.2 Type II System:
Methanol – Cyclohexane – n-Hexane 16
5.3 Strongly Asymetric System:
Water – Phenol – Methanol 17
5.4 Other Types of Phase Behaviour 20

6 Conclusions **21**

References **23**

Nomenclature

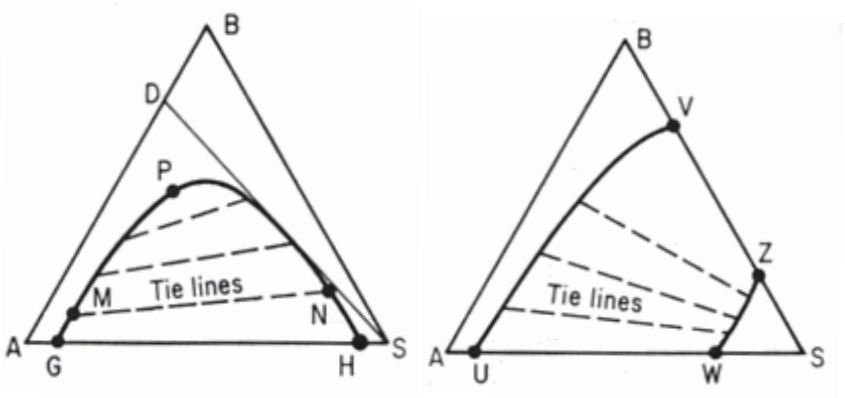
α	Phase rich in Component 1
β	Phase rich in Component 2
γ_i	Activity coefficent for Component i
μ_i	Chemical potential of Component i
x_i	Mole fraction of Component i
A'	Constant used in binary Margules equation
B'	Constant used in binary Margules equation
A'_{ij}	Binary constants used in ternary Margules equation
Q	Ternary constant used in ternary Margules equation

Section 1

Introduction

Solvent extraction is used when ordinary distillation techniques would be ineffective or undesirable, such as when the feed contains heat-sensitive materials, when the two components have a relative volatility near unity or form an azeotope[1 2].

Ternary phase diagrams as shown in figure 1.1 describe the phase behaviour and are used in the design process of solvent extraction equipment[1 2]. This project looks at the construction of such diagrams using known information about the binary systems.



(a) Type I system (b) Type II system

Figure 1.1: Example ternary phase diagrams from Perry[3]

The most common type of phase behaviour is a type I system as shown in figure 1.1a. In this case, the immiscible region touches only one side of the diagram. Figure 1.1b shows a type II system which, whilst not as common as type I systems, are also used for solvent extraction purposes.

Equations to calculate excess Gibbs energies are often used to solve phase equilibria problems. Whilst their use in vapor – liquid equilibria is common, the use of such equations to generate ternary liquid – liquid equilibria from binary data is more difficult[4]. This project uses a ternary form of the Margules equation, as described by Prausnitz[5], to predict the Gibbs energies and hence generate ternary phase diagrams.

The aims of this project were to:

- Carry out a short review to find ternary systems for which data are available.
- Write a JavaScript program to estimate Margules constants.
- Write a JavaScript program to generate ternary LLE data with appropriate simplifying assumption.
- Combine the above, and if practical, adapt existing web browser plotting codes to draw triangular diagrams.

Section 2

The Margules Equation

For two phases to be in equilibrium, the chemical potential for each component, μ, must be equal. So for multicomponent mixtures between two phases α and β:

$$\mu_i^\alpha = \mu_i^\beta \tag{2.1}$$

For ideal systems, the chemical potential can be represented by the mole fraction x_i. The deviation from ideality can be represented by the activity coefficent for that component, γ_i. Therefore, for any given component at equilibrium, equation 2.2 must be true.

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta \tag{2.2}$$

Approximate LLE calculations[6] by Professor Jack Ponton uses the one parameter Margules equation to build ternary diagrams. Using this model requires several assumptions, as discussed on his page, which limit the usefulness of the program.

The two parameter Margules equation was selected to calculate the activity coefficent due to the existence of a ternary form. This two parameter form overcomes some of the short comings of the one parameter program.

Other methods that may be used include the van Laar equations and the Wilson equation[7]. These equations contain just two parameters for a binary system and can be fitted using the two solubility limits similar to how this project collects binary data as shown in section 3.1.

Other modelling systems including NRTL (Non-Random Two Liquid), UNIQUAC (UNIversal QUAsi-Chemical) equations and the UNIFAC method all require extra constants making them unsuitable for this project.

2.1 For Binary System

There are numerous forms of the Margules equation, the form which is used in this program are shown in equations 2.3 and 2.4[5].

$$\ln \gamma_1 = A' x_2^2 + B' x_2^3 \tag{2.3}$$

$$\ln \gamma_2 = \left(A' + \frac{3}{2} B' \right) x_1^2 - B' x_1^3 \tag{2.4}$$

This form of the equation is used to generate the binary data from solubility limits as shown in section 3.1.

2.2 For Ternary System

Equations 2.3 and 2.4 can be manipulated to give the ternary form as shown in equation 2.5.

$$\begin{aligned} \ln \gamma_i = {} & A'_{ij} x_j^2 (1 - 2x_i) + 2A'_{ji} x_i x_j (1 - x_i) + A'_{ik} x_k^2 (1 - 2x_i) \\ & + 2A'_{ki} x_i x_k (1 - x_i) - 2A'_{jk} x_j x_k^2 - 2A'_{kj} x_j^2 x_k \\ & + \left[\frac{1}{2} (A'_{ij} + A'_{ji} + A'_{ik} + A'_{ki} + A'_{jk} + A'_{kj}) - Q \right] (x_j x_k - 2x_i x_j x_k) \end{aligned} \tag{2.5}$$

	γ_1	γ_2	γ_3
i	1	2	3
j	2	3	1
k	3	1	2

Table 2.1: Subscripts used in equation 2.5

The subscripts in equation 2.5 change depending on the γ required and are shown in table 2.1. The constants A'_{ij} in ternary equation 2.5 are related to the constants A' and B' used in the binary equations 2.3 and 2.4 by the relations shown in equations 2.6 and 2.7. Where A' and B' relate to the i–j binary system:

$$A'_{ij} = A' + B' \tag{2.6}$$

$$A'_{ji} = A' + \frac{1}{2} B' \tag{2.7}$$

Equation 2.5 was originally taken from Prausnitz[5] however the equation cited did not yield expected results. Upon further investigation and reading the cited article by Adler[8], it was found that the addition of the term $+A'_{ki}$ into the summation of the Margules constants in the last line fixed the inconsistency.

2.3 Temperature Dependance

It should be noted that the Margules constants are temperature dependant and can be rewritten as shown in equation 2.8. This dependence is used in the enhanced program to model temperature variations.

$$A' = \frac{A}{RT} \tag{2.8}$$

Section 3

Collecting Binary Data

The generation of ternary liquid–liquid equilibria in the program is based on the binary systems. There are a number of ways of obtaining the required data. The equation used requires a ternary parameter, Q; this was set to zero as suggested by Prausnitz[5].

3.1 Solubilities

The generation of ternary graphs is simplified by the process of obtaining data from the solubility limits of two components. The solubility limits are often readily available and where solubility data is not known, the experiment to get solubility data is a relatively simple one compared to the generation of the full ternary diagram by experiment.

At maximum solubility of Component 2 in Component 1, the solution is in equilibrium with the maximum solubility of Component 1 in Component 2. The solubility limit of Component 2 in Component 1, x_2^α, can be used to find the mole fraction x_1^α using the simple binary equation 3.1. This process is also used to get the mole fractions for the β phase.

$$x_2 = 1 - x_1 \tag{3.1}$$

Once all mole fractions are known, values for constants A' and B' can be found. The rewritten equation 2.2 for equilibrium is:

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

Taking *logs* of each side:

$$\begin{aligned} \ln\left(\frac{\gamma_i^\alpha}{\gamma_i^\beta}\right) &= \ln\left(\frac{x_i^\beta}{x_i^\alpha}\right) \\ \ln\gamma_i^\alpha - \ln\gamma_i^\beta &= \ln\left(\frac{x_i^\beta}{x_i^\alpha}\right) \end{aligned}$$

Now substitute in the binary Margules equations (2.3 and 2.4) for $\ln\gamma$ for each component:

$$\begin{aligned} A'\{x_2^\alpha\}^2 + B'\{x_2^\alpha\}^3 - A'\{x_2^\beta\}^2 - B'\{x_2^\beta\}^3 &= \ln\left(\frac{x_1^\beta}{x_1^\alpha}\right) \\ \left(A' + \frac{3}{2}B'\right)\{x_1^\alpha\}^2 - B'\{x_1^\alpha\}^3 - \left(A' + \frac{3}{2}B'\right)\{x_1^\beta\}^2 + B'\{x_1^\beta\}^3 &= \ln\left(\frac{x_2^\beta}{x_2^\alpha}\right) \end{aligned}$$

Which can be rearranged to show that A' and B' are linear:

$$A'\left[\{x_2^\alpha\}^2 - \{x_2^\beta\}^2\right] + B'\left[\{x_2^\alpha\}^3 - \{x_2^\beta\}^3\right] = \ln\left(\frac{x_1^\beta}{x_1^\alpha}\right) \tag{3.2}$$

$$A'\left[\{x_1^\alpha\}^2 - \{x_1^\beta\}^2\right] + B'\left[\frac{3}{2}\{x_1^\alpha\}^2 - \{x_1^\alpha\}^3 - \frac{3}{2}\{x_1^\beta\}^2 + \{x_1^\beta\}^3\right] = \ln\left(\frac{x_2^\beta}{x_2^\alpha}\right) \tag{3.3}$$

3.2 Azeotropes

As mentioned in section 1, solvent extraction and liquid–liquid equilibria are often used when feed components that require separation form an azeotope[2]. The azeotropic data can be used to calculate Margules constants as shown in *Non-Ideal x–y Diagrams*[9]. This was not implemented into the program, however the code has been structured so it may be added later.

Section 4

Program Overview

4.1 Versions of the Program

Two versions of the program were produced— a simple version illustrating the algorithms being used and an enhanced version capable of more accurately modelling real systems.

4.1.1 Basic Version

The main aim of the basic version, as shown in figure 4.1 on page 12, was to show the basic functionality of the program whilst maintaining a simple user interface. The HTML file used in this version was adapted from *Approximate LLE calculations*[6].

This version asks the user to select between type 1 or type 2 systems and enter solubility data for the appropriate binary systems. The remaining binary mixtures are assumed to be ideal. This version only allows mole fractions and the components are prenamed A, B and C. The output can be a right-angled or an equilateral graph which can be easily printed in higher quality.

The basic version was tested on numerous modern web browsers* and no serious problems were noted. The basic version can be accessed online† and is also available on the supplied CD by selecting *basic.html*

*Firefox 2, Internet Explorer 7, Konqueror 3.5.8, Safari 3.1

† `http://www.see.ed.ac.uk/~s0453136/ternary/basic.html`

4.1.2 Enhanced Version

The enhanced version contains several extra features:

- Rename the components
- Handle both mass and mole fractions
- Allow temperature variations
- Handle the entry of Margules constants directly

As with the basic version, the graph can be both right-angled or equilateral and can be viewed in higher quality for printing via the print button.

Due to the increased configurablity in this version, the user interface, as shown in figures 4.2, 4.3 and 4.4 on pages 12–13, was designed to simplify the amount of information on the screen and walk the user through the process rather than showing all the options available to the user at once.

This version was also tested on the same modern web browsers as the basic version and all browsers, with the exception of Internet Explorer, worked with out any issues. Internet Explorer had issues with the code used to hide parts of the user interface, making it unusable. The enhanced version can also be accessed online[‡]

4.2 Structure of Program

The program was primarily based around the code used in *General Non Linear Equation Solver*[10] by Professor Jack Ponton. This uses a basic quasi-Newton method of finite differencing to estimate derivatives of a general non-linear set of equations. The code was edited to solve the set of ternary Margules equations and obtain the end points of a tieline. The procedure is then repeated to get a different tieline.

[‡] `http://www.see.ed.ac.uk/~s0453136/ternary/enhanced.html`

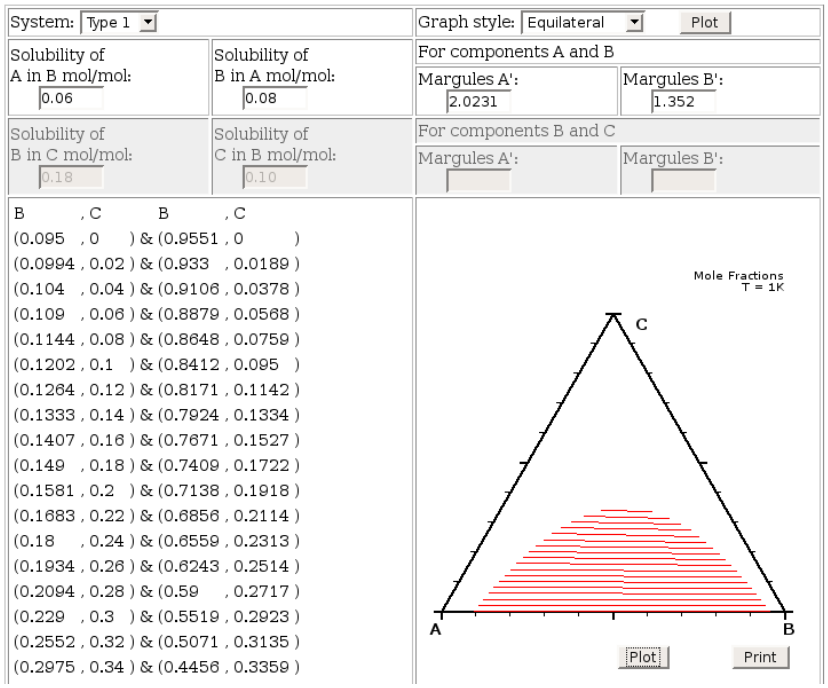


Figure 4.1: Screenshot of the 'basic' program

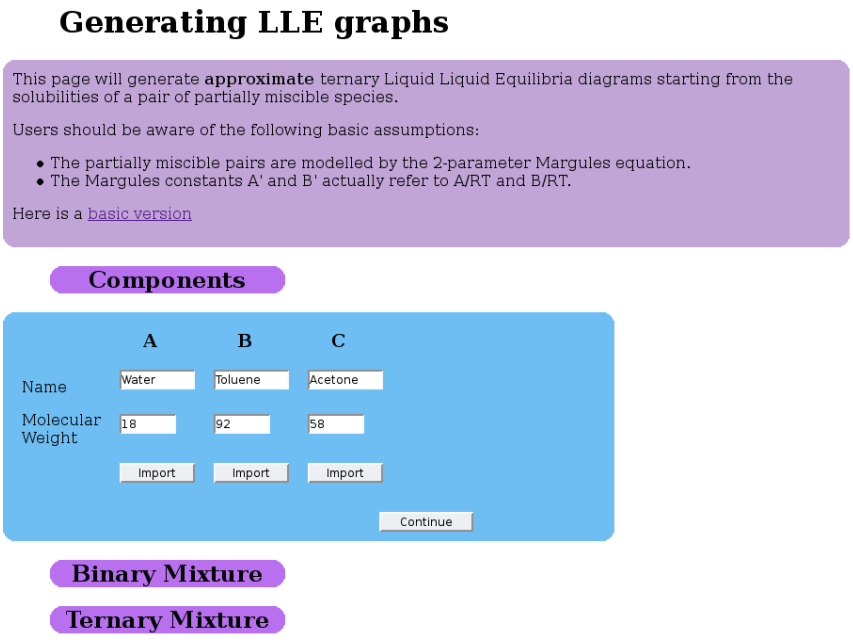


Figure 4.2: Screenshot of the 'enhanced' program: Component information

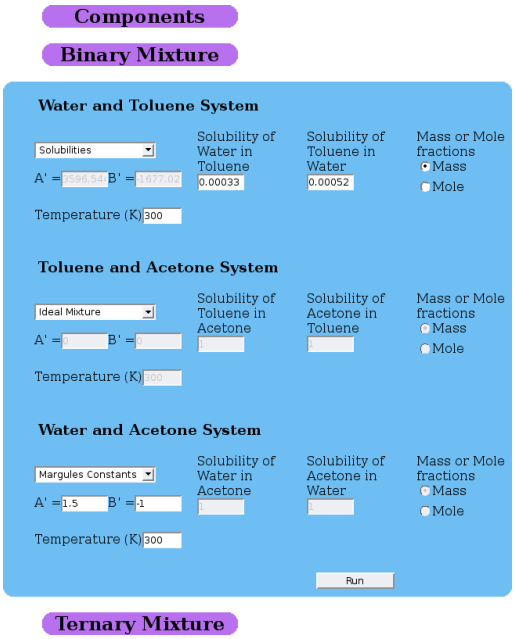


Figure 4.3: Screenshot of the 'enhanced' program: Collecting binary data

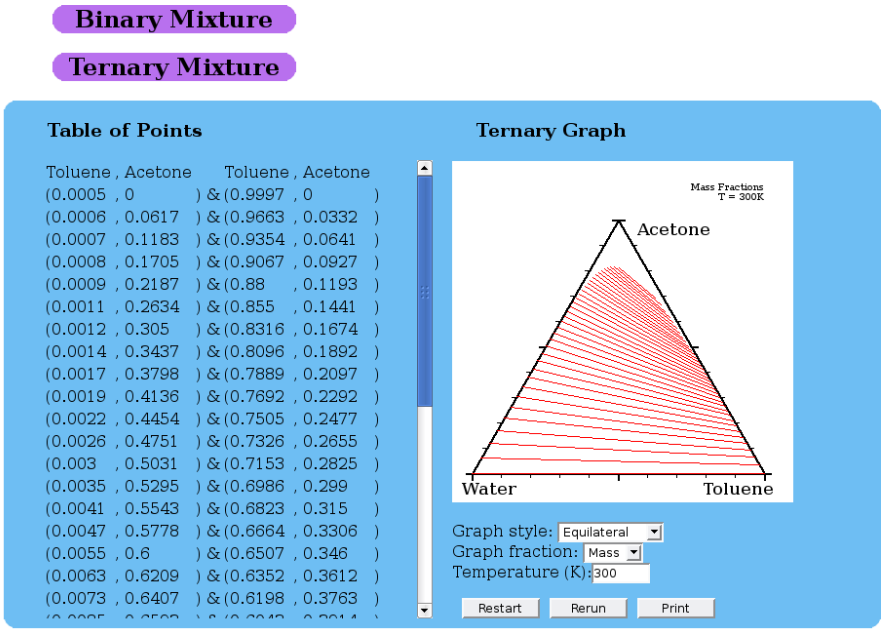


Figure 4.4: Screenshot of the 'enhanced' program: Generating ternary graphs

4.2.1 Directory of files

This section describes the projects files which should be found on the supplied CD and are available for download[§].

`basic.html` Used to define the user interface of the basic version as described in section 4.1.1 and is based on the user interface of *Approximate LLE calculations*[6]

`enhanced.html` Used to define the user interface of the enhanced version as described in section 4.1.2. This file was written solely for this project.

`print.html` Used by both versions to generate the higher resolution graphs prior to printing.

`databank.html` This code has been taken from *Non-Ideal x–y Diagrams*[9] with only minor user interface adjustments being made. It is used to obtain information about chemical substances from a databank. The original `databank.html` file may be used with this program. Similarly, the editions should not break its usage within other projects. This file references other files from elsewhere on the internet which are not included with the program. This file is part of an add-on feature used by the enhanced version and is not required for the core program.

`ternary.js` This file contains the majority of the code written for this project. Its contents are described in section 4.2.2.

`lusby-gauss.js` Used to solve linear equations and is required as part of the non-linear equation solver. This file was used as received and not edited for this project.

`wz_jsgraphics.js` A high performance JavaScript graphics library created by Walter Zorn[11]. This file produces the API used to display the generated ternary diagrams within the webpage. This file was used as received and not edited for this project.

`default.css` This stylesheet is used to define the style of the enhanced program.

`*.png` These image files are used to improve the user interface of the enhanced version.

[§] `http://www.see.ed.ac.uk/~s0453136/ternary`

4.2.2 Description of `ternary.js`

The file `ternary.js` contains the majority of the code written for this project. The first section of this file contains code required to interface with the wz_jsgraphics API. This section supplies functions to draw a blank graph and the drawing of tielines after receiving data from another function.

As mentioned earlier in this section, the program is based around a non-linear solver[10]. The central part of the file contains imported code with edits by myself to enable the program to solve the ternary Margules equation.

The remaining part of this file contains the code which generates the ternary diagrams by collecting the binary data and setting up the ternary equations for the quasi-Newton non-linear solver.

4.3 Calculation of Binary Constants

Currently the program calculates binary constants using the method described in section 3.1. Initially the values were calculated assuming that the equations were not linear and used the quasi-Newton non-linear solver. This brute force method worked for most equations and whilst it was not as efficent as the linear solution, no performance enhancement was noticed after conversion because the non-linear equations involved in the generation of the ternary diagram.

Whilst the non-linear method successfully produced binary constants for most systems, it failed with some binary systems such as toluene–water. In this case, the solubility limits were very low (0.053%, and 0.055% at 25°C[12]) and the Newtonian solver failed to converge. Once the linear method was implemented, the toluene–water system was capable of producing results.

Section 5

Review of Program's Accuracy

This section of the report looks at the graphs generated by the enhanced version of the program and compares them to graphs generated from experemental results found in literature.

5.1 Type I System: Water – Toluene – Methanol

The ternary phase diagram shown in figure 5.1a was taken from a report by L. S. Mason in 1937[13]. The diagram generated by the program shown in figure 5.1b used the solubility limits of water and toluene as found in the IUPAC-NIST solubility database[12]. The water – methanol and toluene – methanol systems were assumed to be ideal. It can be seen that the experimental and modeled graphs produce similar results, though not precise enough for a detailed design procedure.

5.2 Type II System: Methanol – Cyclohexane – n-Hexane

The methanol – cyclohexane – n-hexane system was examined by Paolo Alessi at various temperatures[14]. This type II system allows us to test the program's ability to generate graphs at different temperatures to the reference.

Unlike figure 5.1 for the water – toluene – methanol system which displays the diagram in mass fractions, the diagrams in Alessi's report show mole fractions. The program has been designed so that both systems of measure may be used.

Figures 5.2a, 5.3a, 5.4a and 5.5a were all taken from the paper by Alessi[14]. The modeled diagrams were generated using the solubility limits found in the same paper for the system at $184.15K$ and used the programs temperature variation feature to generate the other ternary diagrams. The cyclohexane – n-hexane was assumed to be ideal.

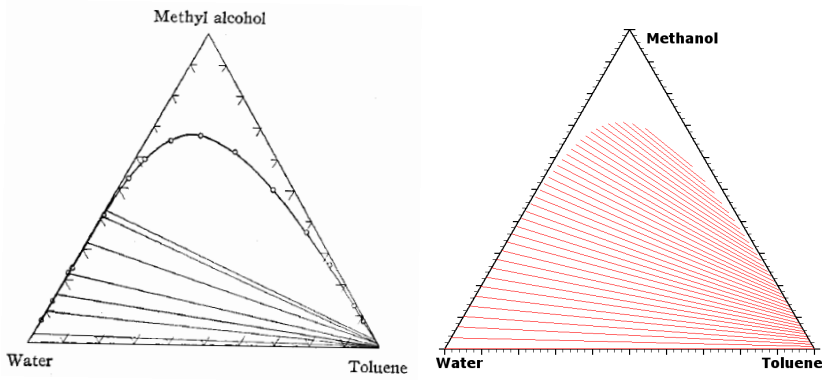
As with the water – toluene – methanol system, the program produced similar but not identical results to those found in the literature. Whilst the graphs produce would be suitable for a rough rule of thumb, they are not accurate enough for detailed design requirements.

5.3 Strongly Asymetric System: Water – Phenol – Methanol

The water – phenol – methanol system, unlike the other systems examined, is heavily skewed. You can dissolve a lot more water in phenol ($28.7\%wt$) than phenol in water ($8.4\%wt$)[15].

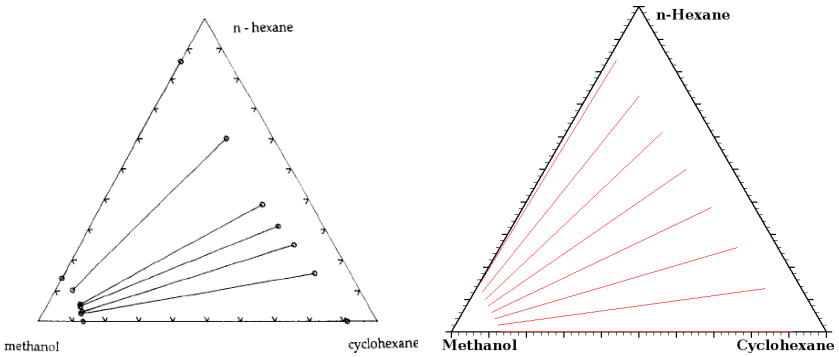
Figure 5.6a is taken from an article by C. F. Prutton on *Solvent Extraction of Tar Acids from Coal Tar Hydrocarbons*[15]. The simulated graph shown in figure 5.6b was created using the solubilities given in the same report and assuming both the water – methanol and phenol – methanol binary systems are ideal.

As can be seen from in figure 5.6 the tielines are not correctly modeled. This may be fixed by removing the assumption that the water – methanol and methanol – phenol systems are ideal and using estimated Margules constants.



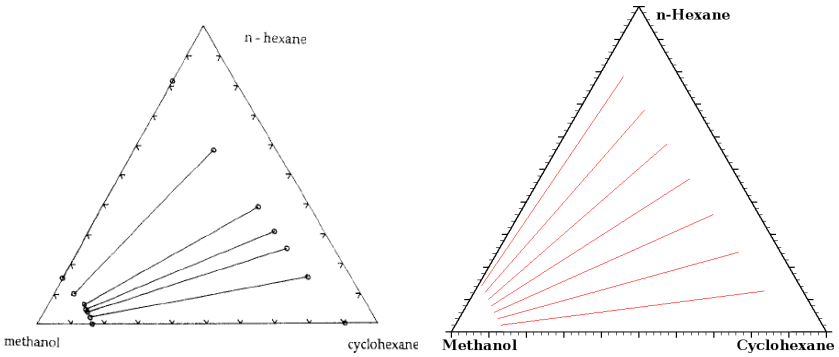
(a) Experemental results. Mason[13] (b) Graph generated from program

Figure 5.1: Ternary graphs for water–toluene–methanol at $25°C$



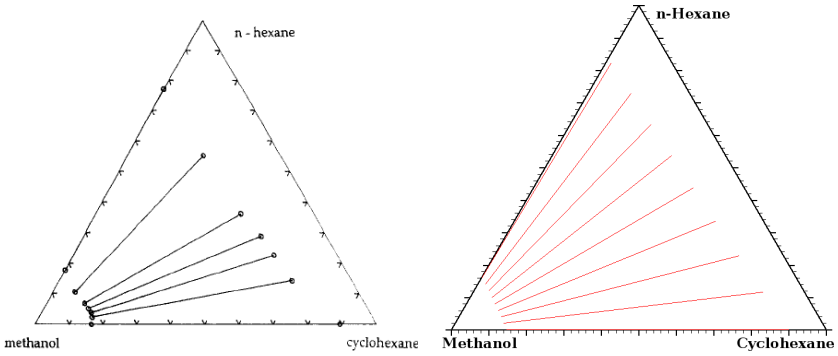
(a) Experimental results. Alessi[14] (b) Graph generated from program

Figure 5.2: Ternary graphs for methanol–cyclohexane–n-hexane at $184.15K$



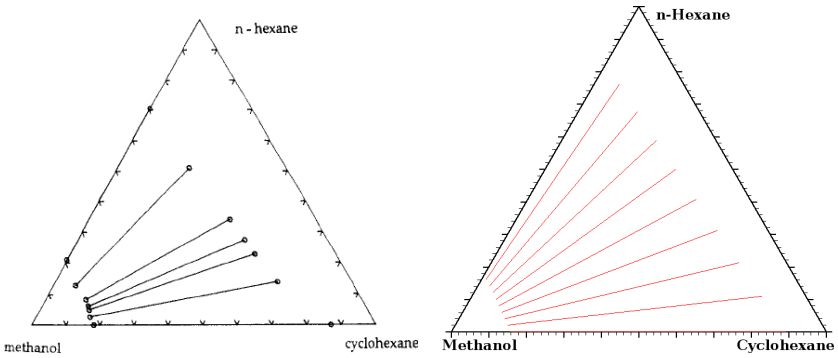
(a) Experimental results. Alessi[14] (b) Graph generated from program

Figure 5.3: Ternary graphs for methanol–cyclohexane–n-hexane at $188.15K$



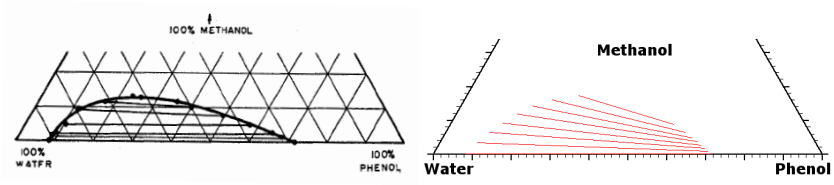
(a) Experimental results. Alessi[14] (b) Graph generated from program

Figure 5.4: Ternary graphs for methanol–cyclohexane–n-hexane at 193.15K



(a) Experimental results. Alessi[14] (b) Graph generated from program

Figure 5.5: Ternary graphs for methanol–cyclohexane–n-hexane at 198.15K



(a) Experemental results. Prutton[15] (b) Graph generated from program

Figure 5.6: Ternary graphs for water–phenol–methanol at 25°C

5.4 Other Types of Phase Behaviour

Beyond the types I and II systems discussed in section 1, several other types of phase behaviour may exist as shown in figure 5.7. These unusual systems are generally undesirable for the operation of extraction[3]. The program was tested for several hypothetical situations however it failed to produce sensible results. It was decided not to attempt to fix the program for these situations due to their limited usefulness in designing extraction systems.

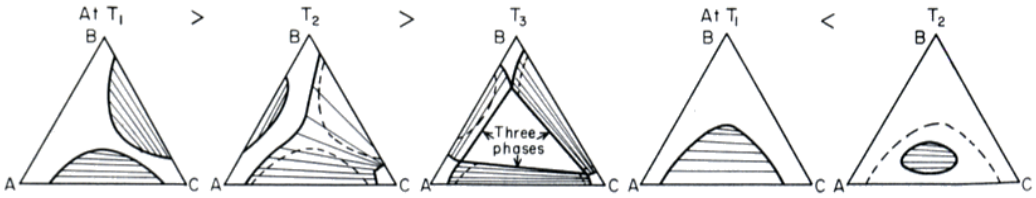


Figure 5.7: Unusual Phase Behavior. Perry[3]

Section 6

Conclusions

The primary aim of this project was to produce a JavaScript program to estimate Margules constants, use these constants to generate ternary liquid – liquid equilibria data and, if practical, plot triangular diagrams. In this regard, the aim has been met and the project can be considered a success. The triangular diagrams produced were comparable to diagrams found in literature in section 5.

As discussed in section 2, other models including the van Laar equations and the Wilson equation may be used, subject to a ternary form of each being found. Further investigation of these models for use in this program was deemed outwith this project's scope.

Whilst this project successfully calculates Margules constants from the mutual solubilities of two liquids, finding available data for these solubilities is often difficult. The solubilities of many substances in water are well documented; however, the solubility of water in other substances is not as well documented. It would be advantageous to calculate the Margules constants from azeotropic data as discussed in section 3.2 because this would not only get around the problem of lack of mutual solubility data but also obtain constants for some completely miscible systems.

As discussed in section 4.1, the program was developed with two user interfaces, basic and enhanced. The basic version worked well and was robust and capable of working with different web browsers. However the enhanced version was not as succesful and as mentioned in section 4.1.2 had several issues with Internet Explorer. It was also noted that whilst the enhanced version attempted to simplify the information presented to the user, many users were still overwhelmed by the different options. This raised the issue of further cluttering the interface should an option be added to calculate Margules constants from azeotropic data. Future work should place more emphasis on the user interface.

Overall, this project has produced a useful program for generating ternary diagrams that can be used as a general rule of thumb. Whilst the generated diagrams should not be used for detailed design of extraction processes, they are effective in demonstrating liquid – liquid phase behaviour.

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