CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Distillation is one of the most common and economical separation process in the industry which involves the separation of the components of a given mixture through the differences in their boiling points. This process is typically applied in the industry in the separation of alcohol-water mixtures, where alcohol is recovered as a pure or concentrated product for specific uses. For example, both ethanol and 2-propanol are separated from water to be used as disinfectants, 1-butanol is recovered as a pure alcohol and used as a fuel additive, and 1-propanol is added in the manufacturing of petrochemical products. A given distillation process can be improved by the addition of mass separating agents (MSA) such as organic compounds and salts. This results to an increase in the volatility of one component and the decrease in the volatility of the other, thereby enhancing the separation process. Because this method of separation is more effective than the separation only by distillation, it is widely applied in the industries.

The improvement of the distillation by the addition of MSAs can also be seen particularly in the biodiesel industry. In the biodiesel production, the salts formed from the formation of alkoxide catalyst such as NaCl and KCl can enhance the separation of the by-product glycerol from the excess methanol or ethanol of the transesterification process. This allows the glycerol to be recovered and the excess methanol or ethanol to be recycled back in the feed for another reaction. Thus, it can be seen that the distillation with MSAs can provides several advantages to industries.

In order to design a distillation column for the separation and purification of a given mixture by distillation, the determination of the vapor-liquid equilibrium (VLE) is important since this process occurs at this equilibrium. This can be possible through the experimental determination of the relationships among the thermodynamic properties of a given mixture such as boiling point, total pressure and liquid and vapor phase compositions at VLE.

However, experiments require a great deal of effort, time and costs. Furthermore, the data from a certain experiment can only be acquired at specific conditions, hence another set of experiments are required if data at other conditions is desired. As an alternative, industries use softwares such as AspenPlus, HYSYS and Comsol, which have with thermodynamic models in their packages that can predict the VLE of a given mixture. Unlike the use of experiments, thermodynamic modelling can be done easily in computers and do not require greater costs from chemicals and equipment, therefore, it is widely performed in industries.

Among the commonly-used thermodynamic models are the group contribution models because of their ability to predict the behavior of a given mixture at VLE even if there is no preliminary experimental data available. Nowadays, the UNIFAC models are the most widely used group contribution models, in which the UNIFAC Dortmund model is the most comprehensive among them so far. The UNIFAC Dortmund model can predict the VLE of wide range of mixtures with the least error in general than the other group contribution models (Muzenda, 2013). According to Gmehling (1995), who developed the model in 1987, the application of this model to a variety of systems resulted to prediction errors that are lower by a factor of 2.5 on average as compared to that of the original UNIFAC (Weidlich and Gmehling, 1987).

Similar to the UNIFAC-based models, the UNIFAC Dortmund model calculates the VLE of a given mixture by identifying the structural group constituents of the components present, which are called subgroups. It is because the model assumes that the subgroups are the interacting species in the mixture and not the components. After determining all the existing subgroups, specific constants that corresponds to these subgroups are used in the calculation, among which are called binary interaction parameters. In the UNIFAC-based models, a binary interaction parameter is a constant that corresponds to a specific binary or pairwise interaction of subgroups in the mixture (e.g. CH_3-OH_p subgroup interaction). Its value depends on the general classification of the subgroups involved in the interaction, which is called the main group. For example, the binary interaction parameters of the subgroup interaction CH_3-OH_p is based on the values provided for CH_2-OH main group

pairs since CH_3 belongs to the CH_2 main group while OH_p or primary OH belongs to the OH main group. Overall, by identifying all the subgroups, their main group classification, and all their possible binary interactions in the mixture, the prediction of VLE data of a given mixture at the desired conditions can be made possible.

To ensure that the UNIFAC Dortmund model is always accurate in predicting VLE data for any mixture, its existing binary interaction parameters which are listed in the UNIFAC Dortmund parameter matrix are constantly being tested and applied to systems with known experimental VLE data in the literature. This is to confirm if the existing parameters can always predict VLE data that are close to the experimental VLE data. For example, Hartanto et al. (2017) showed that the existing parameters for the functional groups in the parameter matrix provided good prediction results for the binary mixtures of alcohols with glycerol as one of the components. On the other hand, Matugi & Giordano (2015) applied the parameters of Aznar & Telles (2001) for various ethanol-water mixtures containing salt as MSA, which also yielded good prediction results. For a wide range of systems in general, the existing parameters can provide accurate predictions of VLE data when compared to experimental VLE data.

However, there are problems that are encountered from the application of the model for some systems. There are cases in which the parameters, when used in the model for the prediction of VLE of certain systems, provide large prediction errors or that the errors they produce can still be minimized. Furthermore, some parameters are absent for certain binary interactions of subgroups, which could have enabled the model to provide good prediction results for some systems. Since these problems are observed, it follows that the UNIFAC Dortmund parameter matrix require certain revisions or further addition or extensions.

For example, the UNIFAC Dortmund binary interaction parameters of Aznar & Telles (2001) involving NaCl and KCl produce average vapor mole fraction prediction errors of at least 0.1 for ethanol-water systems containing the salts mentioned. Thus, these parameters need to be revised to lower their prediction errors in their application to systems with NaCl and KCl. Another example is the absence of some UNIFAC Dortmund binary

interaction parameters involving CNH_2-OH binary interaction in the DDBST website, which are necessary for the prediction of VLE of ethanol + water + TRIS system (DDBST, 2022). These parameters when estimated could potentially provide good prediction results for this system, hence they should be calculated.

These problems that have been mentioned have not yet been addressed specifically in the literatures. Therefore, this study is conducted to address the following problems which aimed at correlating the experimental VLE data of 19 systems using UNIFAC Dortmund model through the revision and addition of UNIFAC Dortmund binary interaction parameters corresponding to the specific subgroups.

1.2 Problem Statement

Various binary, ternary and quaternary systems, with or without salt, require adequate and acceptable parameters for the UNIFAC Dortmund model so that the model can be used for the prediction of VLE data for these systems at various conditions, with a minimum possible error with respect to the experimental VLE data. However, problems in the modelling of the UNIFAC Dortmund model are encountered from other studies such as the necessary revisions of some UNIFAC Dortmund binary interaction parameters involving NaCl and KCl, which provides large prediction errors in the modelling based from the previous study, and the absence of some UNIFAC Dortmund binary interaction parameters for the CNH_2-OH interaction. Hence, the revision and addition of UNIFAC Dortmund binary interaction parameters by correlating the UNIFAC Dortmund model to 19 different systems are to be performed in this study which are aimed to address these problems.

1.3 Objectives

1.3.1 General Objectives

To estimate the parameters and model the vapor-liquid equilibria of various systems with and without mass separating agents.

1.3.2 Specific Objectives

1. To apply the existing UNIFAC Dortmund binary interaction parameters found in the Dortmund Data Bank in the simulation of the activity coefficient and VLE of several types of binary and ternary systems without salt at various conditions.
2. To estimate the new UNIFAC Dortmund binary interaction parameters for CNH_2 – OH interaction for ethanol, water and TRIS system.
3. To modify the binary interaction parameters from the literature for systems with NaCl and KCl.
4. To predict the VLE using the calculated UNIFAC Dortmund binary interaction parameters.
5. To compare the calculated VLE from the experimental and calculated VLE from other studies.

1.4 Significance of the Study

The new binary interactions parameters in this study can be used to predict accurately the VLE of liquid mixtures with or without mass separating agents. It is important to come up with the model of the VLE because most of the time, experimental data are not available. The VLE is essential in the design of distillation columns used for the separation of liquid systems, for example, the production of alcohols and biodiesel from mixtures.

1.5 Scope and Limitations

The UNIFAC Dortmund model was used to predict the VLE of 19 systems considered in this study. Among the 19 systems, 6 binary and ternary systems without salt were used to confirm the existing parameters from the DDBST, 12 binary, ternary and quaternary systems with salt were considered for the revision of the existing parameters involving NaCl and KCl, while the estimation of new parameters for CNH_2-OH interaction the was performed only for the system ethanol + water + TRIS. For the determination of parameters and the calculated VLE of 19 systems using the UNIFAC Dortmund, the study used MATLAB® version 2014a. In this software, the command *fmincon* was used to calculate

the parameters using the sequential quadratic programming optimization method, while the command *rand* was used for the generation of initial guesses for the unknowns. The parameters of Aznar & Telles (2001) were used to obtain another calculated VLE for the purpose of comparison. All the calculated VLE of 19 systems in MATLAB were confirmed using Microsoft Excel 2019.

All the calculated VLE of the systems were compared to their experimental VLE which are found in the literatures as follows: Faggion et al. (2016) for systems with glycerol and/or salt as MSA, Pla-Franco et al. (2013) for ethanol-water systems with glycerol and ethylene glycol as MSA, Bungay et al. (2011) for ethanol-water system with TRIS as MSA, and the studies of Tan & Gan (2005), Tan et. al. (2005) and Tan et. al. (2004) for the quaternary systems.

The study did not consider the application of calculated parameters to systems containing more than 5 types of subgroups and more than 4 components in the parameter estimation, hence the calculated parameters in this study may have limited applicability to these systems. For the parameters that are already present in the UNIFAC Dortmund parameter matrix but were applied in this study, their revision in order to provide better prediction results to the systems considered in this study was not covered.

For the components considered in this study, the functional groups of esters, ketones, aldehydes, etc. were not included but only focused on the components such as alcohols, water and salts. Finally, the salts considered in this study are NaCl and KCl, hence it did not include the other salts whose parameters can also be potentially revised.