Chapter Six

CONCLUSIONS AND RECOMMENDATIONS

The study in general was able to model the VLE of 19 binary, ternary and quaternary systems with and without salt using the UNIFAC Dortmund model through the application, addition, and revision of UNIFAC Dortmund parameters corresponding to the binary interactions present in these systems. For the first objective, the existing parameters from the DDBST were applied in the UNIFAC Dortmund model to test them in the prediction of thermodynamic properties of 6 binary and ternary systems without salt at VLE. It was found out that the application of these parameters provided good prediction of thermodynamic properties for the systems mentioned which are mostly in good agreement with the experimental VLE data. This can also be observed even in the temperature-concentration diagrams created for these systems.

Moreover, new parameters for the CNH_2-OH binary interaction were estimated to improve the prediction of VLE of ethanol + water + TRIS system using the UNIFAC Dortmund model. From the application of the new c_{mk} parameters, it was observed that better prediction results were obtained for the ternary system. To further assess the acceptability of the new parameters, these should be applied to different systems containing the other subgroups of the CH_2NH_2 main group. On the other hand, by observing the liquid-vapor composition diagrams created for this system, the appreciable change in thermodynamic properties with the addition of TRIS cannot be shown using the model. Hence, the model may not be applicable to study the effect of TRIS for this system.

Finally, the existing parameters from the literature for the binary interactions involving NaCl and KCl were successfully revised. The application of the revised parameters to 12 binary, ternary and quaternary systems with NaCl and KCl resulted to the prediction of thermodynamic properties that are mostly consistent with the experimental results, which are better than the existing parameters from the literature. Therefore, the study was able to

demonstrate the applicability of the UNIFAC Dortmund model and to further minimize its errors in the prediction of VLE of various systems with and without salt.

The reasons for the good predictions obtained using the UNIFAC Dortmund model were explored by comparing the molecular interactions predicted by the model to those of the experimental data and to the established theories for the interaction of salts. It was found out that the model was able to describe the interactions in the mixture that are consistent with the order of strength of the different types of intermolecular forces. This was shown when the τ_{mk} values involving water and OH groups are calculated to be the highest while those involving alkyl groups are the lowest, showing that the interactions by hydrogen bonding are the strongest while the interactions involving nonpolar alkyl groups are the weakest.

However, there are few cases where the UNIFAC Dortmund model does not apply for some systems regardless of the parameters used, which were also shown in VLE diagrams. It is because the model does not consider the proximity effects, that is, cases where the interaction of a certain functional group in a given molecule is affected by the neighboring groups in the same molecule. This has been shown in aqueous systems containing components such as glycerol or ethylene glycol, where the effects of their OH groups with each other due to proximity were neglected by the model. This is true even for systems containing chained alcohols such as ethanol, 1-propanol and/or 1-butanol, where the steric effect of the alkyl chain on the OH group is neglected, leading to stronger interaction of OH groups in the mixture. This was especially evident if the mixture contains several ions and highly polar components, which was shown in ethanol + water + propanol + salt systems considered in this study since they contain high percentage of salt and water.

Overall, this study was able to contribute to the revision and extension of the UNIFAC Dortmund parameter matrix, which can be used by various industries to predict the VLE of various systems for distillation applications. Since the estimated parameters in this study were only applied to a limited number of systems, then further application of these parameters to other systems can be performed by future researches to determine the range

of their applicability. Furthermore, since the UNIFAC Dortmund were shown to have limited applicability to some systems, then future researches can perform the addition of new groups and binary interaction parameters in such a way that the prediction of VLE for a given system will not require too much parameters when the UNIFAC Dortmund model is used.