

## Chapter 7 Conclusions

Equations of state play an important role in the prediction of fluid phase equilibria in binary and ternary mixtures. The research on the phase behaviour from equations of state has led to a better understanding of the overall capabilities of equations of state and provided us with a deeper insight in the consequences of intermolecular behaviour on the fluid phase behaviour of binary and ternary systems.

In this work, the van der Waals, Guggenheim and Heilig-Franck equations of state with the van der Waals one-fluid mixing rules have been applied to predict the critical properties and binodal phase equilibria of binary and ternary mixtures. We have found that the Heilig-Franck and Guggenheim equations of state can be used to accurately calculate the critical curves of the ammonia + n-alkane, ammonia + gas, water + noble gas and helium + gas systems with the exception of water + helium. The van der Waals equation has proven to be good in predicting the critical curves of water + helium and helium + gas mixtures, but it can only qualitatively calculate the critical curves for most binary systems. The interaction parameters obtained by optimising the agreement of theory with experiment for the critical properties can be used to predict the isobaric temperature-composition ( $T-x$ ) and isothermal pressure-composition ( $p-x$ ) behaviour. The comparison of theory with experiment demonstrates that the "hard-sphere + attractive term" formulation of either the Guggenheim or Heilig-Franck equations of state is adequate to predict accurately the  $T-x$  binodal curves of binary mixtures containing water and helium. In contrast, the predicted  $p-x$  binodal curves are generally only in qualitative agreement with experimental data. Our work also showed that both vapour-liquid and liquid-liquid equilibria for helium + gas mixtures can be calculated from the same set of combining rule parameters. The predictions using either the Guggenheim or Heilig-Franck equations of state are of similar accuracy. Except in mixtures containing helium, the van der Waals equation generally predicts qualitative agreement with experimental data.

For ternary mixtures, the calculated critical properties of the carbon dioxide + ethylene + helium mixture are in qualitative agreement with the available experimental data. The comparison of theory with experiment also validates the existence of a "double critical point". For the phase behaviour of water + benzene + carbon dioxide ternary mixture, the results also showed qualitative agreement with experimental

curves. Calculations of the critical surface or phase behaviour of the ternary mixtures illustrate the utility of theory to both supplement experimental data and extend our knowledge of multicomponent equilibria. The theoretical study of ternary mixtures of equal size components shows different types of phase behaviour and provides the possibilities for continuing research.

Overall the results, the precision of the calculations for critical properties and binodal phase equilibria in binary and ternary mixtures really depends on the equations of state and mixing rules used. Therefore, the suggestion is that we can use more accurate equations of state, such as APACT, SPHCT or SAFT and incorporate new mixing rules, for example, the Sandler-Wong mixing rule to improve the accuracy of the calculations. It would be very interesting to compare our results with others which will be obtained from these theoretical equations of state and new mixing rules.

There is considerable interest in the prediction of phase equilibria of ternary and multicomponent mixtures. This research just presents a window on the phase behaviour of ternary and multicomponent fluids. The challenge for the future is to improve our ability to predict the phase behaviour of ternary and multicomponent fluid and the most important is to accurately model multicomponent fluids.

## Publications from this thesis

The following papers have been published based on part of this work:

1. Wei, Y. S., Sadus, R. J. and Franck, E. U. (1996) Binary mixtures of water + five noble gases: comparison of binodal and critical curves at high pressures. *Fluid Phase Equilibria*, 123, 1-15.
2. Wei, Y. S. and Sadus, R. J. (1996) Vapour-liquid and liquid-liquid phase equilibria of binary mixtures containing helium: comparison of experiment with predictions using equations of state. *Fluid Phase Equilibria*, 122, 1-15.
3. Wei, Y. S. and Sadus R. J. (1994) Calculation of the critical high pressure liquid-liquid phase equilibria of binary mixtures containing ammonia: Unlike interaction parameters for the Heilig-Franck equation of state. *Fluid Phase Equilibria*, 101, 89-99.
4. Wei, Y.S. and Sadus, R.J. (1994) Critical Transitions of Ternary Mixtures: A Window on the Phase Behaviour of Multicomponent Fluids. *International Journal of Thermophysics*, 15, 1199-1209.