Chapter 7 Conclusions and Recommendations

Both the Guggenheim and Carnahan-Starling-van der Waals equations of state have a hard sphere repulsion term and van der Waals attractive term. The simple van der Waals equation of state can qualitatively predict the phase behaviour of type I to V, but it does not predict type VI phenomena, which is characterised by both lower (LCST) and upper critical solution temperature (UCST) phenomena resulting in closed-loop liquid-liquid immiscibility. The Guggenheim and Carnahan-Starling-van der Waals equations of state in conjunction with the one-fluid model and combining rules for unlike interactions have been applied successfully in the calculation of the critical properties of binary mixtures from type I to VII. This indicates that the closed-loop equilibria can be predicted from hard-sphere + van der Waals interactions. It also indicates, that a reasonably accurate model of hard-sphere interaction is important.

By calculating the global phase diagram of equal size molecules, it was found that type VI, VII and Vm phase behaviour is confined in a narrow range of 1.05 < ? <1.25 and 0.2 < Tr < 0.5. This indicates that for binary mixtures of two pure components with similar molecular size, a large difference in critical temperatures and moderately strong unlike interaction can result in closed-loop equilibria phenomena.

Most previous work on global phase diagrams involved the use of adjustable unlike interaction parameter (? or ?) to represent the contribution of interactions between dissimilar molecules in the binary mixtures. In this work, the global phase diagram was obtained solely in terms of the critical properties of the pure components using the lorentz-Berthelot combining rules. Phase behaviour of Types I to VII were obtained in successfully without the combining rule parameters. This indicates that the critical behaviour of real binary mixtures can be approximately estimated via critical properties of two pure components by using the Carnahan-Starling-van der Waals equation of state, the one-fluid model and the Lorentz-Berthelot combining rules.

The global phase behaviour and diagram of binary mixtures is of considerable interest. There is ample scope for the study of global phase diagrams for the future. Some future challenges include: obtaining type VIII phase behaviour and its location in the global phase diagram; calculating phase behaviour and transitions between different types of behaviour of binary mixtures using molecular simulations; improving the global phase diagram in 3-D space (a, Tr and Vr) using the HCBvdW equation of state and the Lorentz-Berthlot combining rule; and obtaining more accurate equations of state and combining rules.