

Chapter 1 Introduction

Phase equilibrium thermodynamics is one of the most important fundamental sciences for process development in the chemical industry and fluid phase equilibria play an important role in phase equilibria thermodynamics. Over the last decades, the results achieved by many research workers have led to a profound change in predicting fluid phase equilibria. This thesis deals mainly with the prediction of fluid phase equilibria, including critical properties and phase equilibria of binary and ternary fluid mixtures.

1.1 The Role of Phase Equilibria of Binary and Ternary Mixtures

Although the phase behaviour of pure substances is important from both a practical and theoretical point of view, it only represents the limiting behaviour of multicomponent mixtures. Interactions between dissimilar molecules in multicomponent mixtures generate a wide variety of phase transitions which are not observed in pure fluids. Therefore, the phase behaviour of binary and ternary systems is more important in the practical situation because more components coexist. The wealth of phenomena displayed by binary and ternary systems is illustrative of the complexity of multicomponent phase equilibria.

The use of physical property models in process development is more economic than the process development which is based on experiments. However, this depends on the availability of physical property models. In our work, equations of state are investigated with respect to the prediction of fluid phase equilibrium in binary and ternary fluid mixtures. There are two goals to be achieved in this work. One is the comparison of predicted binary and ternary phase behaviour with experimental data. Another one is that our results can provide an insight into the general fluid phase behaviour of multicomponent systems and the complicated world of phase behaviour.

The phase behaviour of fluid mixtures is very diverse and depends on the characteristics of the individual components and their respective interactions. For binary mixtures, the shape of the critical curves can be used to classify phase equilibria. The most commonly used systematic classification was proposed by van Konynenburg and Scott (1980). They based their work on the analysis of the van der Waals equation of

state using the one-fluid mixing rules. Their results were summarised in a global phase diagram, which was projected onto the pressure-temperature (p - T) projection. For ternary systems, a completely diagrammatic representation of the effects of pressure, temperature and composition is considerably more complicated. Walas (1985) discussed the phase behaviour according to the numbers and kinds of presented phases. Sadus (1992) reported the some types of critical transitions based on a phenomenological interpretation of critical calculations.

1.2 Progress in High Pressure Prediction Fluid Phase Equilibria

Most of the experimental and theoretical work has concentrated on binary mixtures (see Chapter 5). The study of binary mixtures is valuable in understanding the behaviour of multicomponent mixtures because it elucidates the role of interactions between unlike molecules. The theoretical analysis of binary mixtures is well documented (Sadus, 1992, 1994) and considerable effort has been made to predict the critical state and phase equilibria behaviour.

The earliest attempts to predict critical properties (Grievess and Thodos, 1962, Redlich and Kister, 1962, Rowlinson, 1969) involved either empirical correlations or approximate solutions of the critical conditions. The usefulness of this approach was restricted to the gas-liquid critical properties and even the quantitative analysis of many of these mixtures was unsatisfactory. Deiters and Swaid (1984) attempted to calculate liquid-liquid properties by extending the criteria for equilibrium between homogeneous phases to the critical state. However, a general solution is required to calculate all possible aspects. Around the same period, various perturbation (Fischer and Lago, 1983), lattice gas (Andersen and Wheeler, 1979), *ad hoc* (Deiters and Schneider, 1976) and the conformal solution theory (Hicks and Young, 1975) models were developed. The conformal solution theory is possibly the most widely used model for phase equilibria calculations, particularly at high temperatures and pressures (Sadus, 1992).

An equation of state is almost invariably incorporated into the chosen model. The first "theoretical" equation based on the pressure-volume-temperature properties to predict the coexistence of vapour and liquid was proposed by van der Waals. Subsequently, better models were developed by Redlich and Kwong (1949), Soave (1972), Guggenheim (1965), Carnahan and Starling (1969) and others. Adjustable parameters are a common feature of most equations of state. The parameters, for

theoretical equations of state, usually represent some physical property of the fluid, like molecular volume, shape and attractive forces. Because the prediction of pure component properties is the natural starting point for the development of an equation of state, techniques must be developed to extend it to mixtures. This is most commonly achieved by proposing mixing rules and combining rules for the adjustable parameters. Therefore, the prediction of phase equilibrium behaviour is limited by both the accuracy of the equation of state and the method used to obtain its adjustable parameters for the mixing and combining rules. Over the last decades, various equations of state and mixing rules have been being well developed. For details refer to Chapter 3.

The work of Spear et al. (1969) represents, possibly, the first attempt to rigorously calculate critical equilibria with realistic equations of state. Hicks and Young (1977) developed a robust algorithm for calculating equilibria of binary systems. Van Konynenburg and Scott (1980) showed that the van der Waals equation could be used to qualitatively predict most aspects of the phase behaviour of binary mixtures and a similar analysis was made for the Redlich-Kwong equation (Deiters and Pegg, 1989). Since then, based on different equations of state and mixing rules, various predictions of critical transition and phase equilibria behaviour have been reported. Vidal (1984) and Elliot and Daubert (1987) reported that the Soave equation of state can adequately predict the gas-liquid critical properties of binary mixtures containing hydrocarbons. Mainwaring et al. (1988) applied both the Guggenheim (1965) and the Deiters (1981) equation of state in conjunction with conformal solution theory, the van der Waals one-fluid mixing rules and the Lorentz combining rule to the prediction of the gas-liquid critical properties of 46 binary mixtures. Sadus et al. (1988) reported a similar analysis of the gas-liquid critical properties of 61 binary mixtures using the Guggenheim equation and the hard convex body (HCB) equation of state of Svejda and Kohler (1983). Christou et al. (1989, 1991a, 1991b) calculated the gas-liquid critical temperatures of weakly polar halocarbons + hydrocarbon and 26 1-alkanol + n-alkane mixtures and compared the results with experiment. Comprehensive reviews on the progress achieved in calculating the critical transitions of both binary and ternary mixtures are available (Sadus, 1992, 1994).

Recently, effort has been devoted to calculating critical and phase equilibrium properties by using the various improved equations of state and mixing rules. Van Nhu and Kohler (1995) and Van Nhu and Deiters (1996) applied a generalized van der Waals equation of state (Van Nhu et al., 1993) with improved mixing rules to 30

nonpolar binary mixtures and reported good agreement for vapour-liquid and liquid-liquid equilibria over a large temperature range. Economou and Tsonopoulos (1997) have used three different equations of state (Associated Perturbed Anisotropic Chain Theory --- APACT, Statistical Associating Fluid Theory --- SAFT and Redlich-Kwong-Joffe-Zudkevitch --- RKJZ) to obtain an accurate description of water/hydrocarbon phase equilibria. In Castier and Sandler's (Castier and Sandler, 1997) work, the Stryjek and Vera version (Stryjek and Vera, 1986) of the Peng-Robinson equation of state (Peng and Robinson, 1976) and the modified NRTL model (Huron and Vidal, 1979) were combined using the Wong-Sandler (Wong and Sandler, 1992) mixing rules. Castier and Sandler (1997) compared their critical point calculations results with experimental data for some highly non-ideal binary mixtures, such as n-alkane + 1-alkanol, n-pentane + acetone, carbon dioxide + water, water + n-dodecane and methane + n-hexane. The results showed that this combination was able to quantitatively predict the critical behaviour of some highly non-ideal binary systems. Blas and Vega (1998) applied their modification version of SAFT equation of state (Blas and Vega, 1997) to predict thermodynamic properties, as well as liquid-vapour equilibria, of binary and ternary mixtures of hydrocarbons. Comparing their results with experimental data, they concluded that their version of SAFT equation of state can correctly predict the phase behaviour of binary and ternary mixtures.

1.3 Outline of Thesis

The theory of fluids is of fundamental importance to the prediction of fluid phase equilibria. In chapter 2, a review for conformal solution theory and perturbation theory will be given. The van der Waals one-fluid and multi-fluid models will be discussed in detail. The Barker-Henderson (Barker and Henderson, 1967) and Weeks-Chandler-Andersen (Weeks et al., 1971) and their modified perturbation theories will be reviewed. Perturbation theory for associating fluids is also reviewed.

It is well known that equations of state play a central role in chemical engineering design. Various equations of state will be detailed in chapter 3, including equations of state for simple molecules, chain molecules and associating fluids. An equation of state is commonly used in conjunction with a fluid theory. Mixing and combining rules are also reviewed in this chapter.

Chapter 4 deals with the criteria of phase equilibrium for binary and ternary mixtures. Details of the Newton-Raphson method and the Hicks-Young algorithm used in this work to calculate both binodal and critical equilibria for binary and ternary mixtures are discussed.

In Chapter 5, details of the phase equilibria calculations of some binary systems (ammonia + simple gases or n-alkanes, helium + non-polar gas and water + 5 noble gases) will be presented. The unlike interaction parameters of the van der Waals one-fluid mixing rules for binary mixtures will be obtained by comparing experimental critical data with calculation results using the van der Waals, Guggenheim and Heilg-Franck equations of state. These interaction parameters and equations of state will be used to predict *a priori* either vapour-liquid, liquid-liquid or so-called gas-gas equilibria and produce a series of binodal diagrams. The predicted critical curves in p - T projection and binodal diagrams in p - x or T - x projections will be given and compared with experimental data for a wide range of pressures, temperatures and compositions.

Chapter 6 will discuss some results for ternary mixtures about critical transitions ($\text{CO}_2 + \text{C}_2\text{H}_4 + \text{He}$) and phase equilibria behaviour ($\text{H}_2\text{O} + \text{C}_6\text{H}_6 + \text{CO}_2$). The purpose of the analysis is to illustrate how the calculation of ternary critical transitions and phase equilibria behaviour can prove an insight into the general fluid phase behaviour of multicomponent mixtures. A theoretical study of ternary mixtures of equal size components are also reported.

Finally, in Chapter 7 conclusions and an outlook on the possible future research in related subjects will be given.

References

- Andersen, G. R. and Wheeler, J. C. (1979). Two-Component Lattice-Gas Model with a Liquid-Vapour Phase Transition in both Pure Components. *J. Chem. Phys.*, **70**, 1326-1336.
- Barker, J. A. and Henderson, D. (1967). Perturbation Theory and Equation of State for Fluids. II. A Successful Theory of Liquids. *J. Chem. Phys.* **47**, 4717-4721.

- Blas, F. J. and Vega, L. F. (1997). Thermodynamic Behaviour of Homonuclear and Heteronuclear Lennard-Jones Chains with Association Sites from Simulation and Theory. *Mol. Phys.*, **92**, 135-150.
- Blas, F. J. and Vega, L. F. (1998). Prediction of Binary and Ternary Diagrams Using the Statistical associating Fluid Theory (SAFT) Equation of State. *Ind. Eng. Chem. Res.*, **37**, 660-674.
- Carnahan, N. F. and Starling, K. E. (1969). Equation of State for Nonattracting Rigid Spheres. *J. Chem. Phys.*, **51**, 635-636.
- Castier, M. and Sandler, S. I. (1997). Critical Points with the Wong-Sandler Mixing Rule --- II. Calculations with a Modified Peng-Robinson Equation of State. *Chem. Eng. Sci.*, **52**, 3579-3588.
- Christou, G., Sadus, R. J., Young, C. L. and Svejda, P. (1989). Gas-Liquid Critical Properties of Binary Mixtures of n-Alkanes and 2,2,4-Trimethylpentane with the Weakly Polar Halocarbons 1,2-Dichloroethane, cis-1,2-Dichloroethene, trans-1,2-dichloroethane, and Tetrachloromethane. *Ind. Eng. Chem. Res.*, **28**, 481-483.
- Christou, G., Sadus, R. J. and Young, C. L. (1991a). Phase Behaviour of 1-Alkanol + Alkane Mixtures: Gas-Liquid Critical Temperatures. *Fluid Phase Equilib.*, **67**, 259-271.
- Christou, G., Young, C. L. and Svejda, P. (1991b). Gas Liquid Critical Temperatures of Binary Mixtures of Polar Compounds + Hydrocarbons or + other Polar Compounds. *Ber. Bunsenges. Phys. Chem.*, **95**, 510-514.
- Deiters, U. K. (1981). A New Semiempirical Equation of State for Fluids. I. Derivation. *Chem. Eng. Sci.*, **36**, 1139-1146.
- Deiters, U. K. and Pegg, I. L. (1989). Systematic investigation of the phase behaviour in binary fluid mixtures. I. Calculations based on the Redlich-Kwong equation of state. *J. Chem. Phys.*, **90**, 6632-6641.
- Deiters, U. K. and Schneider, G. M. (1976). Fluid Mixtures at High Pressures. Computer Calculations of the Phase Equilibrium and the Critical Phenomena in Fluid Binary Mixtures from the Redlich-Kwong Equation of State. *Ber. Bunsenges. Phys. Chem.*, **80**, 1316-1321.
- Deiters, U. K. and Swaid, I. (1984). Calculation of Fluid-Fluid and Solid-Fluid Phase Equilibria in Binary Mixtures at High Pressure. *Ber. Bunsenges. Phys. Chem.*, **88**, 791-796.

- Economou, I. G. and Tsonopoulos, C. (1997). Associating Models and Mixing Rules in Equations of State for Water/Hydrocarbon Mixtures. *Chem. Eng. Sci.*, **52**, 511-525.
- Elliott, J. R. and Daubert, T. E. (1987). Evaluation of an Equation of State Method for Calculating the Critical Properties of Mixtures. *Ind. Eng. Chem. Res.*, **26**, 1686-1691.
- Fischer, J. and Lago, S. (1983). Thermodynamic Perturbation Theory for Molecular Liquid Mixtures. *J. Chem. Phys.*, **78**, 5750-5758.
- Grieves, R. B. and Thodos, G. (1962). The Critical Temperature of Multicomponent Hydrocarbon Systems. *AIChE J.*, **8**, 550-553.
- Guggenheim, E. A. (1965). Variations on van der Waals' Equation of State for High Densities. *Mol. Phys.*, **9**, 199-200.
- Hicks, C. P. and Young, C. L. (1975). The Gas-Liquid Critical Properties of Binary Mixtures. *Chem. Rev.*, **75**, 119-175.
- Hicks, C. P. and Young, C. L. (1977). Theoretical Prediction of Phase Behaviour at High Temperatures and Pressures for Non-polar Mixtures. Part 1. Computer Solution Techniques and Stability Tests. *J. Chem. Soc., Faraday Trans. II*, **73**, 597-612.
- Huron, M. J. and Vidal, J. (1979). New Mixing Rules in Simple Equation of State for Representing Vapour-Liquid Equilibria of Strongly Nonideal Mixtures. *Fluid Phase Equilib.* **3**, 255-271.
- Mainwaring, D. E., Sadus, R. J. and Young, C. L. (1988). Deiters's Equation of State and Critical Phenomena. *Chem. Eng. Sci.*, **43**, 459-466.
- Peng, D. Y. and Robinson, D. B. (1976). A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **15**, 59-64.
- Redlich, O. and Kister, A. T. (1962). Thermodynamics of Solutions. VII. Critical Properties of Mixtures. *J. Chem. Phys.*, **36**, 2002-2009.
- Redlich, O. and Kwong, J. N. S. (1949). On the Thermodynamics of Solutions. V: An Equation of State. Fugacities of Gaseous Solutions. *Chem. Rev.*, **44**, 233-244.
- Rowlinson, J. S. (1969). *Liquids and Liquid Mixtures*. Butterworths, London, 2nd Ed.
- Sadus, R.J. (1992). *High Pressure Phase Behaviour of Multicomponent Fluid Mixtures*, Elsevier, Amsterdam.
- Sadus, R. J. (1994). Calculating Critical Transitions of Fluid Mixtures: Theory vs. Experiment. *AIChE J.*, **40**, 1376-1403.

- Sadus, R. J., Young, C. L. and Svejda, P. (1988). Application of Hard Convex Body and Hard Sphere Equations of State to the Critical Properties of Binary Mixtures. *Fluid Phase Equilib.*, **39**, 89-99.
- Soave, G. (1972). Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.*, **27**, 1197-1203.
- Spear, R. R., Robinson, Jr. R. L. and Chao, K. C. (1969). Critical States of Mixtures and Equations of state. *Ind. Eng. Chem. Fundam.*, **8**, 2-8
- Stryjek, R. and Vera, J. H. (1986). PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures. *Can. J. Chem. Eng.*, **64**, 323-333.
- Svejda, P. and Kohler, F. (1983). A Generalized van der Waals Equation of State: I. Treatment of Molecular Shape in Terms of the Boublik Nezbeda Equation. *Ber. Bunsenges. Phys. Chem.*, **87**, 672-680.
- Van Nhu, N., Iglesias-Silva, G. A. and Kohler, F. (1993). An Equation of State for Non-polar Substances Based on the Generalized van der Waals Model. *Fluid Phase Equilib.*, **91**, 215-237.
- Van Nhu, N. and Kohler, F. (1995). Excess Properties and Phase Equilibria Calculated from a Generalized van der Waals Equation of State for the Example of the Mixture Methane + Ethane. *Fluid Phase Equilib.*, **105**, 153-171.
- Van Nhu, N. and Deiters, U. K. (1996). Application of a generalized van der Waals Equation of State to Several nonpolar Mixtures. *Fluid Phase Equilib.*, **118**, 153-174.
- Van Konynenburg, P. H. and Scott, R. L. (1980). Critical Lines and Phase Equilibria in Binary van der Waals Mixtures. *Phil. Trans. Roy. Soc. London A*, **298**, 495-540.
- Vidal, J. (1984). Phase Equilibria and Density Calculations for Mixtures in the critical Range with Simple Equations of State. *Ber. Bunsenges. Phys. Chem.*, **88**, 784-791.
- Wala s, S. M. (1985). *Phase Equilibria in Chemical Engineering*. Butterworth, Boston.
- Weeks, J. D., Chandler, D. and Andersen, H. C. (1971). Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids. *J. Chem. Phys.*, **54**, 5237-5247.
- Wong, D. S. H. and Sandler, S. I. (1992) A Theoretically Correct Mixing Rule for Cubic Equation of State. *AIChE J.*, **38**, 671-680.