

Chapter 1 Introduction

1.1 Aims

The aim of this work is to examine the phase behaviour of binary mixtures via the calculation of critical properties. In particular, we use the critical properties of binary mixtures to develop a global phase diagram.

A global phase diagram is a two-dimensional map which identifies regions of different phase behaviour depending on the properties used for the x and y coordinates. A feature of most theoretical global phase diagrams is that they involve the use of unlike interaction terms to represent the contribution of interactions between dissimilar molecules in the mixture.

Our aim is to investigate both the use of different properties for the coordinates and the effect of different equations of state on the global phase diagram.

1.2 The Role of Critical Phenomena of Binary Mixtures

The critical state provides a valuable insight into the general phase behaviour of a fluid and is closely linked with the nature and strength of intermolecular interaction (Sadus, 1994). Many applications of materials science, chemistry and biophysics are concerned with the properties of multi-component systems. Extraction, adsorption and distillation are essential operations in the chemical industry, and understanding of any one of them is based on the study of phase equilibria and critical properties of

mixtures. Over the last decades, work on both experimental and theoretical aspects of the critical phenomena of binary mixtures has developed greatly.

A rich variety of critical phenomena are observed for binary mixtures. The critical point is reached when coexisting phases become indistinguishable, in terms of any physical property (Sadus, 1992; Prausnitz et al., 1999). For pure fluids, the pressure, temperature and volume of coexisting liquid and vapour phases are identical at the vapour-liquid critical point. The vapour-liquid critical point is the only critical state for a pure fluid. In contrast, mixtures of two or more components generate a wide variety of critical phenomena involving both vapour-liquid and liquid-liquid equilibria (Schneider, 1978; McGlashan, 1985).

The most important illustration of the role of the critical state is the phase behaviour classification proposed by van Konynenburg and Scott (1980). There are six main types of critical curves in the pressure-temperature projection (see Chapter 2, figure 2.1). These types of critical curves can be located on a global phase diagram, the details of which are discussed in Chapter 4.

1.3 Progress in Calculating Critical Properties

The theoretical analysis of binary mixtures is well documented and considerable effort has been made to predict the critical state (Sadus, 1992). Most of the experimental and theoretical work has concentrated on binary mixtures (Wei, 1998). The study of binary mixtures is valuable in understanding the behaviour of multi-

component mixtures because it elucidates the role of interactions between unlike molecules.

The earliest attempts to predict critical properties (Redlich and Kister, 1962, Rowlinson, 1969) involved either empirical correlation or approximate solutions of the critical conditions. The usefulness of this approach was restricted to vapour-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. Various perturbation (Fisher 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 have been developed. Among them, the theory of conformal solutions (Brown, 1957) is possibly a 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 (1873). Attempts to improve the van der Waals equation of state were made by Redlich and Kwong (1949), Soave (1972), Peng and Robinson (1976), Guggenheim (1965), and Carnahan and Starling (1969).

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. Mainwaring et al. (1988) applied the Guggenheim (1965) and the Deiters (1981) equations 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 vapour-liquid critical properties of binary mixtures. Sadus et al. (1988) reported a similar analysis of the vapour-liquid critical properties of binary mixtures using the Guggenheim equation and the hard convex body (HCB) equation of state (Svejda and Kohler, 1983). Comprehensive reviews on the progress achieved in calculating the critical transitions of binary mixtures are available (Sadus, 1992, 1994). 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 non-polar binary mixtures and reported good agreement for vapour-liquid and liquid-liquid equilibria over a large temperature range. Polishuk et al. (1999) compared the critical lines predicted by six cubic equations of state and classical mixing rules with the experimental data of the mixtures of methane and an alkane.

Recently, effort has been devoted to calculating critical properties by simple, accurate and various improved equations of state. Sadus (1999a, 1999b) derived both simple hard-sphere chain (HSC) and hard convex body chain (HCBC) equations of state

using thermodynamic perturbation theory, and the accuracy of the HSC equation is tested against simulation data for hard-sphere chains containing up to 201 hard-sphere segments. Yelash and Kraska (2000) developed a biquadratic equation of state for the attractive hard sphere chain fluid with dipolar interactions for a simplified mathematical form. Kiselev et al. (1996) introduced a crossover equation of state, which incorporates the scaling laws asymptotically close to the critical point and which is transformed into the regular classical expansion (Kiselev, 1998, Cubic; Kiselev and Ely, 1999, SAFT; Wyczalkowska et al., 1999, van der Waals EOS) far away from the critical point of binary mixtures.

Since the first global phase diagram for binary mixtures (van Konynenburg and Scott, 1980) based on the van der Waals equation of state, there have been many newer ones. A global phase diagram is a two-dimensional map, which identifies regions of different phase behaviour in accordance with the properties of the x and y coordinates. Critical transitions of different kinds generate boundary lines between different types of phase behaviour. Binary mixtures that exhibit multi-critical points, double critical end points, and other phenomena form the boundaries between the various regions in a global phase diagram. Valuable insight can be obtained by examining the differences in the global phase behaviour between various fluid models.

Deiters and Pegg (1989) studied the global phase behaviour of the Redlich-Kong equation on the effects of size differences between the components. Kraska and Deiters (1992) obtained similar results by employing the Carnahan-Starling-Redlich-Kwong equation. Van Pelt et al. (1993) studied the global phase behaviour of the simplified-perturbed-hard-chain equation and also took the effects of dissimilar

flexibility of the two components into account. Yelash and Kraska (1998) obtained closed-loop diagrams by combining the Carnahan and Starling hard-sphere equation of state (1969) with the original van der Waals attraction. Wang et al. (2000) employed the Guggenheim equation of state to predict successfully closed-loop liquid-liquid equilibria phase behaviour. Canongia Lopes (1999) used a three-box version of the Gibbs ensemble Monte Carlo to determine the phase diagram type of several binary mixtures of one-centre Lennard-Jones particles. Yelash and Kraska (1999) investigated the global phase behaviour of binary mixtures from small non-spherical and short chain molecules to long chain polymer molecules.

1.4 Outline of thesis

In Chapter 2, a review of classical and non-classical aspects of critical phenomena will be given. For non-classical critical behaviour, we will introduce the concept of critical exponents which provides an insight into the nature of the critical transition. We will also give a detailed description of classification of critical phenomena of binary mixtures, and of criteria for critical equilibrium and calculation procedure.

Hundreds of equations representing the PVT behaviour of fluids have been proposed a few before van der Waals but mostly later. They have a central role in the thermodynamics of fluids. The investigation of equation of states also is an important part in our research. Equations of state for high pressure are reviewed in Chapter 3.

By making a thorough investigation and study fluid phase equilibria of binary mixtures, more and more phase behaviour are found and analysed, this led to the

global phase diagram based on the van der Waals equation of state being obtained (van Konynenburg and Scott, 1980). This has recently been extended by Yelash and Kraska (1998) and Wang et al. (2000) by using the Carnahan-Starling and Guggenheim equations of state, respectively. A review of global phase diagram is found in Chapter 4.

In Chapter 5, calculations of the critical properties of binary mixtures of components of equal size are reported using the Guggenheim equation of state. The calculations are used to determine the global phase diagram of binary mixtures. Type VI phase behaviour is predicted successfully indicating that closed-loop liquid-liquid equilibria can be obtained from hard sphere + van der Waals interactions. Closed-loop liquid-liquid equilibria occur in the region of the global phase diagram characterized by moderately strong unlike interactions and for components with very dissimilar critical temperatures. The Guggenheim equation can predict all experimentally known phase behaviour types. In addition, other hypothetical phase behaviour types are also predicted.

Chapter 6 will discuss binary mixtures with components of greatly different critical properties. The phase behaviour of mixtures is governed directly by intermolecular interactions both between similar and dissimilar molecular entities. In normal circumstances for mixtures of molecules of relatively similar size the relative energy of interaction plays the dominant role in determining the phase behaviour. Other influences such as molecular shape and size that contribute only indirectly to the intermolecular interactions generally play a minor role. Both the experimental study and calculation of critical points has proved to be an effective way of classifying the

phase behaviour of binary mixtures. Different categories of phase behaviour can be assigned depending, for example, on whether the vapour-liquid critical line is continuous or interrupted or whether upper critical solution phenomena are observed. However, our understanding of the phase behavior of mixtures is confined largely to mixtures containing components of relatively similar shape and size. In this work, we report calculations of critical phenomena of hypothetical mixtures containing molecules of vastly different critical properties. The results, which have implication for mixtures containing molecules such as dendrimers and very long chain polymers, indicate a rich diversity of phase equilibrium and novel critical behavior.

In the last part chapter 7 of this thesis, we will give the conclusion of our work and an outlook on the possible future research in related subjects.

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