CHAPTER I

INTRODUCTION

1.1 General

Thermodynamic characteristics of vapour-liquid phase equilibria are of significance in a number of chemical and physical processes which include distillation, absorption, and fractional condensation. An adequate knowledge of equilibrium compositions, temperatures, and pressures of vapour-liquid systems and availability of reliable correlations for their prediction, are essential for feasibility studies and successful design of equipment for separation processes and in the interpretation of the operation and performance of existing industrial plants.

With an ever increasing number of complex vapour-liquid equilibrium problems arising from numerous new industrial processes, there is a need for more rapid and accurate methods in the determination and prediction of vapour-liquid equilibria. Both the experimental measurements and the development of predictive methods are complimentary to each other. It is necessary to have data of one kind or other for the evaluation of parameters appearing in the thermodynamic equations. One may consider why vapour-liquid equilibrium data are not measured directly whenever need arises for such data. Experimental measurements of vapour-
liquid equilibria is not an easy task even for binary systems. Considerable experimental skill, experience, and patience are required. The experimental effort increases very rapidly with the complexity of the system. This is reflected in the fact that most of the equilibrium data presently available are for binary systems. With the development of analytical techniques it has become now possible to determine vapour-liquid equilibria for systems involving more than three components. However data on such systems are extremely rare.

Thus there is a strong incentive for the development of predictive methods, especially for multicomponent systems. It would be ideal if predictive methods, which require only pure component properties, are developed. Such advances were made in this direction in recent years with limited success but this objective appears to be unrealistic at the present moment especially when one considers that the nature of interactions between identical molecules would be rather different from those between unlike molecules. With the present state of understanding of the theories of solutions, it therefore appears reasonable to expect that some mixture properties would be required for any realistic predictive method. Thus, the predictive method must require only a limited amount of experimental data and should be based on a theoretical foundation in order to be reliable for interpolation and extrapolation with respect to temperature, pressure, and composition. There has been considerable progress, especially in recent years, in the development of methods for the
prediction and correlation of vapour-liquid equilibria. Such developments are being greatly aided by the increasing use of digital computers for the rapid evaluation of thermodynamic parameters which are then used for obtaining complete information on the behaviour of vapour-liquid systems. With the aid of computers it is now possible to rapidly test the thermodynamic consistency of experimental equilibrium data by applying various tests and apply some of the complex correlating and predicting equations in both binary and multicomponent systems. Properties of multicomponent systems can be predicted with reasonable accuracy from constituent binaries.

1.2 Scope of the Thesis

Tremendous amount of attention has been paid, over a number of years to the subject of vapour-liquid equilibria both for the experimental determinations and development and comparison of theoretical methods for the prediction and correlation of vapour-liquid equilibria. Yet there is no universal method that can predict or correlate vapour-liquid equilibria with equal accuracy for all types of systems. There is a continuing need for obtaining reliable data on different types of mixtures which serve as a basis for different predictive methods. This is one of the objectives of this thesis. The other objectives are:

a) to determine vapour-liquid equilibria for some important near-ideal and nonideal systems including those with the constituent components having widely differing boiling points and those that given rise to azeotropes,
b) to assess the effect of vapour-phase nonideality on vapour-liquid equilibria at atmospheric and near-atmospheric pressure;

c) to study the vapour-liquid equilibria of C₈ aromatic compounds with different types of nonhydrocarbon compounds as part of an overall research programme for the development of experimental data for the individual components of close-boiling mixtures and different types of nonhydrocarbon compounds which will be of use in the development of special distillation techniques for the separation of close-boiling hydrocarbon mixtures which otherwise require elaborate separation equipment;

d) to develop digital computer programmes (i) for the evaluation of different predictive methods for pure component properties such as vapour pressures, second virial coefficients, and liquid molar volumes which are relevant in the determination of activity coefficients and vapour phase nonidealities, (ii) for assessing the thermodynamic consistency of binary and ternary experimental data, and (iii) for testing the suitability of various correlations for binary and ternary systems.

Petroleum fractions especially from the catalytic reforming processes are one of the major sources of C₈ aromatics. Xylenes and ethylbenzene form close-boiling mixtures, with p-xylene and ethylbenzene forming the closest boiling pair with about 2°C
difference in the boiling points. At present these are separated by fractionation using very large number of stages and high reflux ratios or by fractional crystallisation involving elaborate equipment and other processing problems. Knowledge of vapour-liquid equilibria between ethylbenzene or p-xylene and different classes of compounds will be of importance in the development of alternative distillation processes for their separation. Vapour-liquid equilibrium data at atmospheric pressure were obtained for six binary systems in which one component is either ethylbenzene or p-xylene and the second component is either a chlorinated compound or an ether or an aldehyde (Work with other types of compounds is in progress).

The system cyclohexane - isopropylbenzene, has thermodynamic importance because of the large difference in the boiling points (71.73°C) of the pure components. The contribution of the vapour phase nonideality to the activity coefficients at normal pressures depends mainly on the difference in boiling points of the pure compounds and hence study of this system would be of use in assessing the vapour-phase nonideality. Moreover, very high purity isopropylbenzene especially required for the manufacture of nylon, is obtained from petroleum sources which contain cyclohexane together with other compounds. Vapour-liquid equilibrium data on this system, therefore, will be of use in the design and interpretation of the distillation process employed for its separation.
The systems, methanol - 1,2-dichloroethane and 1,2-dichloroethane-methylcyclohexane, have thermodynamic and technical importance. These systems can be expected to give rise to large deviations from ideal solution behaviour giving rise to azeotropes. Data on these systems will be of importance in the evaluation of separation processes and thermodynamic predictive methods.

The system, methanol - benzene - 1,2-dichloroethane, is interesting because one of the constituent binaries, namely, benzene - 1,2-dichloroethane is ideal and the other two binaries give rise to positive azeotropes. Data on this type of systems consisting of dissimilar polar-nonpolar mixtures is of great importance in testing multicomponent thermodynamic correlations using mostly data on the constituent binary systems.