CHAPTER I

INTRODUCTION
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The properties of binary mixtures are of considerable interest (1,2,3,4), both from the practical and theoretical point of views. Chemical engineers and chemists need the data on binary mixtures for design purposes. Theoretical chemists and physicists require the information for comparing the properties of binary mixtures predicted on the basis of the characteristics of the molecules constituting the mixture or conversely from the observed properties they try to find out the nature of the interaction between the molecules. The multiple attraction for the subject has been the meeting ground for the scientists from the different disciplines and there has been considerable activity to develop the subject both on the experimental and theoretical fronts.

Progress on the experimental side has led to better design of calorimeters, accurate measurement of vapour pressure, volume and its dependence on temperature and pressure. Realising the importance of using pure chemicals, workers have paid due attention to the purification of the chemicals which has been possible by some recent analytical techniques. Earlier method for estimating the excess free energy by measuring total vapour pressure and determining the composition both in liquid and gas phases has given way to a much simpler method in which only the composition in
the liquid phase and total vapour pressure are required. The procedure for calculations involving least squares and iteration in its present form has been proposed by Barker (5). The method has been used in various laboratories (6,7) with success and modern computation aid has further facilitated the calculations. We have followed Barker's method throughout this work for estimation of excess free energy. The earlier method of determining excess enthalpy by knowing the temperature dependence of excess free energy has fallen out of grace due to large uncertainties involved. Direct calorimetric determinations are to be preferred.

On the theoretical side, complete prediction of the properties of liquid mixtures from the molecular properties seems to be an uphill task. Besides the inherent difficulties of the problem of liquid state there are added complexities due to increase in the number of components and inter-molecular interaction between molecules of different types. The complete solution of the problem being a distant possibility at present, the theoreticians are contented with the prediction of the properties of mixing (difference between the properties of solution and pure components) of the excess functions (properties of mixing for a real solution - properties of mixing for an ideal solution). Significant progress has been made in this direction and a number of molecular theories (3,8-15) of mixtures have been formulated. However, much of the success of these
theories has been limited to binary mixtures whose components consist of non-polar spherical molecules. The studies have been extended even to molecules of irregular shapes and even to that of polymer solutions, but not with much success for example in spite of an arbitrary constant the theoretical predictions by Flory (16 - 20) for n-hydrocarbons in a number of solvents are not in agreement with the experimental results.

There is a great paucity of data for mixtures in which the shape and the size have been varied systematically. The results reported in thesis constitute the first report from this laboratory where work has been started on the thermodynamic properties of short chain n-alkanes in different solvents. The study reports the total vapour pressure for the systems n-hexane/benzene, n-heptane/benzene, n-hexane/carbon tetrachloride, and n-heptane/carbon tetrachloride over a range of temperatures. The data have been used for the calculations of excess free energy and its temperature dependence has been used to calculate excess enthalpy. The excess volumes have been determined for these systems by other workers (20a, 20b) in this laboratory. The experimentally determined values for various excess functions are compared with those calculated from different theories.