CHAPTER - 1

INTRODUCTION
1. INTRODUCTION

In recent years there has been a considerable upsurge in the theoretical and experimental investigations of the vapour-liquid equilibria and excess thermodynamic properties of binary and multicomponent mixtures. These excess thermodynamic functions, which depend on the composition, temperature and pressure of the system, describe behaviour of liquid mixtures which is of great importance to a chemical engineer in the design of industrial separation processes and to a chemist for arriving at theories of liquid solutions. The physical, chemical and thermodynamic properties associated with the liquids and liquid mixtures like viscosity, excess molar volume, compressibility, enthalpies of mixing, vapour-liquid equilibria and liquid-liquid equilibria directly depend upon the nature of the molecules that constitute it, so a thorough knowledge of molecular behaviour is, therefore, essential to understand completely the physical or chemical behaviour of a substance. In principle, the interaction between the molecules can be established from a study of the characteristic abrupt departure from ideal behaviour of some physical properties like volume, compressibility and viscosity. The study of these properties is used as a tool for investigating the properties of the mixture and the nature of intermolecular interactions between the components constituting the mixture.

Vapour-liquid equilibrium studies are important because they serve as a basis for the success of many operations like distillation, both azeotropic and extractive, gas absorption, humidification and dehumidification and many chemical reactions which are carried out with a gas or vapour in intimate contact with the liquid phase. The techniques for calculation and experimental determination of this particular type of phase equilibria are highly developed due to its vast applications. The experimental determination of vapour-liquid equilibria received a boost since the development of the first successful equilibrium still with circulating vapour phase by Othmer [264], which has remained to be popular with experimentalists even today in one form or the other.

With an ever increasing number of complex vapour-liquid equilibrium problems arising from numerous new industrial processes, there is a need for the accurate vapour-liquid equilibrium determinations experimentally, which even for a binary system are most tedious, time consuming and require lot of skill and patience.
So in the face of the difficulties which are encountered in the experimental determination, it becomes necessary to think of some predictive methods having theoretical foundation and preferably based on the pure component or mixture properties, so as to get the complete equilibrium data or to extend the data from one set of conditions to another. A considerable amount of work has already been done in this field but still there is enormous scope for further work to develop general fool proof methods to account for deviations caused by physical, chemical and size effects, especially for non-ideal mixtures involving associating components. The developments are being greatly aided by the increasing use of computers for the rapid evaluation of thermodynamic parameters especially for multi-component systems, which are then used for obtaining complete information on the behaviour of vapour-liquid equilibrium systems. Also computers facilitate the testing of the data for thermodynamic consistency.

Knowledge of the viscosities of liquid mixtures is indispensable in many practical problems concerning transport operations. Viscosity data for liquid mixtures have also yielded information regarding the nature of interaction forces between the molecules [181] and the existence of complex [84, 97, 391], if any. Many attempts have been made to interpret viscosity data empirically [126, 127, 156, 162]. Bloomfield and Dewan [35] have examined the expressions connecting the viscosities of binary liquid mixtures with their thermodynamic properties, using the concept of absolute reaction rate theory as well as free volume theory of flow. However, there seems to be no reliable theoretical method to estimate these viscosities, as many viscosity-composition curves are non-linear functions of compositions.

There have also been a number of studies on the measurement of ultrasonic velocities and isentropic compressibilities of liquid-liquid mixtures. The deviations from the rectilinear dependence of ultrasonic velocities and compressibilities on the mole fractions throw much light on the physico-chemical behaviour of liquid mixtures such as molecular association and dissociation as well as the strength of interactions between the components. It has been found that a number of derived parameters from ultrasonic velocity such as isentropic compressibility, intermolecular free length etc. provide better insight in the understanding of molecular interactions in pure liquids and binary or ternary mixtures.
Parallel to the increased activity in the measurement of the thermodynamic properties of liquid mixtures, there has also been a rapid proliferation in the number of theoretical treatments. A number of these are based on an equation-of-state approach [77, 82, 178, 330], which differ by variations in the equation and the combining rules. Other approaches are based on interaction parameters and seek to relate the properties of one mixture to those of closely related mixtures or mixtures formed from constituent groups. A very common approach is to correlate the measured values of excess properties by algebraic expressions of mole fractions with arbitrary, temperature-dependent coefficients, which are obtained by fitting experimental data. Thermodynamic properties of liquid mixtures can be related to several measurable physical properties such as vapour pressure, heat capacity etc. and thus can be easily determined. Thermodynamic properties of mixing may also be related to the molecular properties through the methods of statistical mechanics – a branch of science which on one hand depends on the behaviour of atoms and molecules and on the other hand is related to macroscopic properties of the system. The ultimate aim of all these efforts is to predict excess properties from the pure component properties without any experimental knowledge of the actual system itself.

The deviations of a mixture in terms of properties of mixing, when determined, can be utilized to understand the molecular behaviour of components and conclusion can be drawn regarding the intermolecular forces existing between the constituent molecules. If however, as in most practical situations, the deviations are significant and their magnitude is not even predictable, one must resort to experimental measurements to determine the real behaviour of the solution. Thus experimental determination of properties of mixing help in understanding the exact behaviour of molecules of components in mixtures, which is ultimately helpful in accurate and fail-safe design and operation of modern chemical plants.

1.1 Objectives of the Present Investigation

From the literature review, it seems that little experimental work on \( C_8 \) hydrocarbons as one of the components has been reported. Such components form industrially important combinations in petroleum and petrochemical industries. In view of their close boiling point and varied binary interactions, separation becomes difficult.
In order to have a better insight of binary interactions, it was desirable to study the interactions involved and to determine the vapour-liquid equilibrium data of such mixtures having C₈ hydrocarbon (p-Xylene) as one of the components and the other component with varying polarity. The type and extent of interactions influence the vapour-liquid equilibrium data and correlation between the two was worth investigating.

In order to fulfill these objectives, detailed investigation of the following systems was conducted:

<table>
<thead>
<tr>
<th>System</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Xylene – n-Decane</td>
<td>Non Polar – Non Polar</td>
</tr>
<tr>
<td>p-Xylene – Triethylamine</td>
<td>Non Polar – Slightly Polar</td>
</tr>
<tr>
<td>p-Xylene – Isoamyl Acetate</td>
<td>Non Polar – Medium Polar</td>
</tr>
<tr>
<td>p-Xylene – Vinyl Acetate</td>
<td>Non Polar – Medium Polar</td>
</tr>
<tr>
<td>p-Xylene – 1-Octanol</td>
<td>Non Polar – Highly Polar</td>
</tr>
<tr>
<td>p-Xylene – 2-Nitrotoluene</td>
<td>Non Polar – Highly Polar</td>
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</table>

The main objectives of the present investigation are:

- To experimentally measure excess volume, viscosity and ultrasonic velocity of binary mixtures at different temperatures involving p-Xylene as one of the components.
- To calculate densities of mixtures from the experimental excess volume data.
- To experimentally measure the isobaric vapour-liquid equilibrium data at 730 ± 2 mm Hg pressure for binary mixtures involving p-Xylene as one of the components and to evaluate the activity coefficients.
- To evaluate the excess properties such as deviations in viscosity and excess isentropic compressibility.
- To test and enhance predictability of various models/equations.
SECTION-I

VAPOUR-LIQUID EQUILIBRIUM