CHAPTER 1

INTRODUCTION
1. INTRODUCTION

In recent years, vapor-liquid equilibrium has drawn much attention both from theoretical and practical point of view in chemical industries, particularly petroleum and petrochemical industry. Experimental determinations of vapor-liquid equilibrium are indispensable for the design of distillation columns and the selection of solvents. Separation of liquid mixtures by distillation is one of the most important processes in chemical industries. One of the problems often encountered in the field of separation technology is the separation of close-boiling liquid mixtures. Conventional distillation for such mixtures necessitates large number of stages and use of high reflux ratio resulting in high equipment and operating cost. Use of third component in an extractive and azeotropic distillation process reduces the cost of separation by bringing in a change in the relative volatility between the components to be separated.

The techniques for calculation and experimental determination of vapor-liquid equilibrium are highly developed due to its vast applications. The experimental determination of vapor-liquid equilibrium received a boost since the development of the first successful equilibrium still with circulating vapor phase by Othmer [185], which has remained to be popular with experimentalists even today in one form or the other. Due to complex vapor-liquid equilibrium problems arising from numerous new industrial processes, there is a need for the accurate vapor-liquid equilibrium determinations experimentally. In addition to this, experimental data are required to update and improve the data bank used to fit the model parameters of various theoretical models. Vapor-liquid equilibrium data provides information about the composition dependence of the activity coefficients. Data of activity coefficient at infinite dilution not only gives information about temperature dependence of activity coefficients but also describe the real phase behaviour in the dilute region. The data is also of great industrial interest as it can be directly used for choosing selective solvent for the extractive distillation.

All the compounds being studied have a wide range of application and are of great industrial importance. Cumene, also known as isopropyl benzene, is used to manufacture other chemicals such as phenol, acetone, acetophenone and methyl styrene. It is used as a thinner in paints, lacquers and enamels. Also, it is a component
of high-octane motor fuels. Natural sources of cumene include crude petroleum and coal tar.

Cyclic ethers are used as important solvents, chemical intermediates and monomers for ring-opening polymerization. They are unstable at room temperature due to possibility of peroxide formation; stabilizer is sometimes needed for storage and transportation. Tetrahydrofuran is an industrial solvent and a chemical intermediate widely recognized for its unique combination of useful properties. It is used as a resin solvent in PVC top coating, printing ink for plastics, cellophane coatings, as a reaction solvent for Grignard’s reagent, steroids and high molecular weight organic polymers, as a chemical intermediate for polytetramethylene ether glycols and natural gas odorants. Selected alkylated analogs of tetrahydrofuran and tetrahydropyran are used as solvents for electrolytes in batteries having alkali metal negative electrodes. Methyltetrahydrofuran is used as a specialty solvent and as a reactant for the production of chemicals including 2-methylpyrrolidine and \(N\)-substituted 2-methylpyrrolidines. Methyltetrahydrofuran is a more convenient solvent than tetrahydrofuran for Grignard reagents; it is higher boiling and wet. Methyltetrahydrofuran is more easily recovered and made anhydrous for recycle and reuse. It is also used as a solvent for other organometallic reagents as well as for electrolytic solutions in lithium batteries.

\(N, N\)-dimethylacetamide is a very effective solvent used in separation technology. Furthermore, it is a very good polymer solvent, dissolving polyacrylates and polyesters.

Ethyl formate is used for the synthesis of vitamin \(B_1\) and as a flavor in the food industry. It is also used as a solvent for acetyl cellulose and nitrocellulose. Methyl acetate, also known as methyl ethanoate, is a clear, flammable liquid with a characteristic, not unpleasant smell like certain glues or nail polish removers. Methyl acetate has characteristics very similar to its analog ethyl acetate. Methyl acetate is used as a solvent in glues and nail polish removers, in chemical reactions and for solvent extractions. Methyl acetate is a non-polar (lipophilic) to weakly polar (hydrophilic) aprotic solvent. Methyl acetate has a solubility of 25% in water at room temperature. At elevated temperature its miscibility with water is much higher. Methyl acetate is not stable in the presence of strong aqueous bases or acids. Vinyl
acetate monomer is a chemical building block used to manufacture a wide variety of polymers including: polyvinyl acetate; polyvinyl alcohol; polyvinyl acetals; ethylene vinyl acetate copolymers; and ethylene vinyl alcohol. These polymers are commonly used in the production of plastics, films, lacquers, laminating adhesives, elastomers, inks, glue, acrylic fibers, paper coatings, floor tiling and safety glasses.

\textit{n-Butyl amine} is used as an intermediate in the synthesis of dyes, drugs, rubber additives, emulsifiers, tanning agents and insecticides. It is also used as a vulcanizing accelerator for rubber and as a curing agent for polymers. Triethylamine is commonly employed in organic synthesis as a base, most often in the preparation of esters and amides with acyl chlorides. Such reactions lead to the production of hydrogen chloride which combines with triethylamine to form the salt triethylammonium hydrochloride, commonly called triethylammonium chloride. This reaction removes the strongly acidic hydrogen chloride from the reaction mixture, which can otherwise lead to side reactions. Triethylamine is also used for the preparation of quaternary ammonium compounds and in the synthesis of pesticides, pharmaceuticals, paints and coatings. As a catalyst, it is used to help cross-linking of polyurethane foams and also for the synthesis of epoxy and phenolic resins. Other applications of triethylamine include curing, hardening and corrosion inhibition for polymers and its use as a propellant.

The experimental determination of vapor-liquid equilibrium, even for a binary system is tedious, time consuming and require lot of skill and patience, thereby giving an impetus to development of predictive tools / theoretical models (ASOG, UNIFAC) 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. With the revision of the group interaction parameters, the extension of the parameter matrix (introduction of new structural groups, filling of parameter gaps) and the help of a large database, the predicted results of the group contribution methods have significantly improved and the range of applicability greatly extended. 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 vapor-liquid equilibrium systems. Also computers facilitate the testing of the data for thermodynamic consistency.

1.1 Objectives of the Present Investigation

From the literature review, it is clear that little data has been reported on the binary mixtures containing cumene as one of the components. Such components form industrially important combinations in chemical industries. In order to understand the degree of non-ideality, it is proposed to study the isobaric vapor-liquid equilibrium at 730 ± 2 mm Hg for the following class of systems:

1. Cumene + Cyclic ethers
2. Cumene + Esters
3. Cumene + Amines
4. Cumene + Amides

The different compounds selected from each class of systems have varying degrees of polarity and chemical structures. This choice has been made to determine the effect of chemical structure on the phase equilibrium in addition to the effect of polarity. As significant difference exists among the structures of various compounds of the same group, a noticeable difference in the phase equilibrium is expected to exist.

The main objectives of this work are:

- To experimentally measure the isobaric vapor-liquid equilibrium at 730 ± 2 mm Hg for the above listed combinations.
- To check the consistency of the experimental data and to generate activity coefficient data and excess Gibbs free energy data from the experimental measurements.
- To study the degree of non-ideality in the systems selected and to check if various combinations produce azeotropic mixtures.
- To correlate the data with Margules, NRTL, Black and Wilson equations and to find the constants and root mean square deviations by using the standard methods.
- To check the predictive ability of group contribution models.
COMPONENT 1: Cumene (Isopropylbenzene)

Dipole moment = 0.39 Debyes, Refractive index at 25 °C = 1.48890

COMPONENT 2

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Main group</th>
<th>Compound name</th>
<th>Molecular Formula</th>
<th>Dipole-moment</th>
<th>Refractive-index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cyclic ether</td>
<td>Tetrahydrofuran</td>
<td>C₄H₈O</td>
<td>1.75</td>
<td>1.40496</td>
</tr>
<tr>
<td>2.</td>
<td>Cyclic ether</td>
<td>Tetrahydropyran</td>
<td>C₆H₁₀O</td>
<td>1.63</td>
<td>1.41862</td>
</tr>
<tr>
<td>3.</td>
<td>Cyclic ether</td>
<td>2-Methyltetrahydrofuran</td>
<td>C₇H₁₀O</td>
<td>*</td>
<td>1.40508</td>
</tr>
<tr>
<td>4.</td>
<td>Ester</td>
<td>Ethyl formate</td>
<td>C₂H₄O₂</td>
<td>1.94</td>
<td>1.35750</td>
</tr>
<tr>
<td>5.</td>
<td>Ester</td>
<td>Vinyl acetate</td>
<td>C₄H₆O₂</td>
<td>1.79</td>
<td>1.39340</td>
</tr>
<tr>
<td>6.</td>
<td>Ester</td>
<td>Methyl acetate</td>
<td>C₃H₆O₂</td>
<td>1.72</td>
<td>1.35890</td>
</tr>
<tr>
<td>7.</td>
<td>Amine</td>
<td>n-Butylamine</td>
<td>C₄H₁₀N</td>
<td>1.37</td>
<td>1.39870</td>
</tr>
<tr>
<td>8.</td>
<td>Amine</td>
<td>Triethylamine</td>
<td>C₆H₁₅N</td>
<td>0.87</td>
<td>1.39800</td>
</tr>
<tr>
<td>9.</td>
<td>Amide</td>
<td>N-Methylacetamide</td>
<td>C₇H₁₂NO</td>
<td>4.27</td>
<td>1.42860**</td>
</tr>
<tr>
<td>10.</td>
<td>Amide</td>
<td>N,N-dimethylacetamide</td>
<td>C₇H₁₄NO</td>
<td>3.71</td>
<td>1.43560</td>
</tr>
</tbody>
</table>

* Not available in literature
** Refractive Index at 28 °C