VAPOUR LIQUID EQUILIBRIUM STUDIES
IN BINARY SYSTEMS
Vapour-liquid equilibrium studies are important due to the fact that these serve as a basis for the success of many mass transfer operations like distillation inclusive of azeotropic and extractive processes, gas absorption, humidity control systems and many chemical reactions which are carried out with a gas or vapour in intimate contact with the liquid phase. The importance and influence of petroleum processing industry, the rapid growth of petrochemical industry, the increased requirements for pure liquid compounds, increased emphasis on pollution control processes and the lack of understanding of the liquid phase have contributed to
the continued interest in vapour-liquid equilibrium studies.

For quantitative design calculations in distillation, it is necessary to have reasonably accurate vapour-liquid equilibrium data. These might be obtained by a variety of methods like

i. direct experimental determination
ii. calculation using few experimental data sets to determine constants in semi-theoretical correlations
iii. calculation using vapour pressure data and assuming ideal behaviour
iv. estimation from molecular structure and other physical data on pure components with the use of empirical relationships.

Though a number of theories have been proposed for describing the gas phase but no satisfactory theory which is universally applicable for describing the liquid phase has been developed, mainly because of complexity in the nature of intermolecular forces that exist in liquid systems. As a result one can not completely avoid time-consuming experimental determination of vapour-liquid equilibria, which are essential for accurate design calculations in distillation.

Voluminous amount of work has been done in the past on the estimation of activity coefficients to describe the nonideal behaviour of vapour-liquid systems. Most of the times, the contribution of the vapour phase to activity coefficients has been neglected, on the assumption that at low pressures the vapour phase behaves ideally. In many cases this is justified but in
certain types of systems this contribution is too significant to be neglected. This is especially true with systems having large difference in boiling temperatures and systems with components which are known to associate in vapour phase. Interest in such systems has increased in recent times.

This work is a part of a programme, undertaken in this laboratory, to study vapour-liquid equilibria, heats of mixing and other excess thermodynamic properties for systems involving close-boiling hydrocarbons and nitrocompounds, alcohols and aliphatic acids.

The principal objective of the present investigation is to explore the possibility of using highly polar compounds, like aliphatic acids, as separating agents in azeotropic or extractive distillation of the close boiling C₉ aromatics. The conventional processes for separation of such mixtures involve either the use of unwieldingly tall distillation towers or fractional crystallisation methods involving cumbersome solid handling processes. The other objectives are

a) to determine experimentally vapour-liquid equilibrium data for mixtures of aliphatic acids and aromatic hydrocarbons at normal pressures, to be used in the development of quantitative methods for the separation of such mixtures,

b) to extend Nethagel's approach for calculating activity coefficients in such systems, to verify its validity,

c) to evaluate the parameters in various correlating equa-
tions and to assess the data fit in these correlations for acid-hydrocarbon systems,

d) to compare the various methods of calculating activity coefficients by utilizing experimental data on such nonpolar-highly polar mixtures, which are available in literature and
e) to develop a reliable predictive method for aseptropic conditions in such mixtures.

Major sources of C8 aromatics are petroleum fractions. Catalytic reforming processes give petroleum fractions containing ortho-xylene, meta-xylene, paraxylene and ethylbenzene. Xylenes and ethylbenzene form close-boiling mixtures, with ethylbenzene and paraxylene forming the closest boiling pair with about 2°C difference in boiling points.

Pure ethylbenzene is required in the manufacture of styrene by catalytic dehydrogenation and pure xylenes are used as industrial solvents and in the manufacture of chemicals like xyldines, phthalic acid, phthalic anhydride etc. At present separation of pure ethylbenzene or of pure xylene from petroleum fractions is done 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 paraxylene and different classes of compounds will be of importance in the development of alternative distillation processes for their separation. Isopropylbenzene is required for the manufacture of nylon and is also obtained from
petroleum sources. Vapour-liquid equilibrium data at atmospheric pressure were obtained for ten binary systems in which one component is a C₈ aromatic compound and the second is an aliphatic acid.