INTRODUCTION

1.1 General

The measurement of enthalpies of mixing has become an important part in the theoretical and experimental study of equilibrium properties of liquid mixtures in the recent years. In the last few years tremendous amount of data has been published on excess thermodynamic properties since the concept was first introduced by Scatchard[209] in 1931. These properties are proving to be increasing useful. The recent spurt in the research activity in this field is due to the importance of these variables in the design of separation equipments and better understanding of interactions among molecules which will ultimately lead to better predictive and correlative methods for thermodynamic properties.

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 functions of mixing may also be related to the molecular properties of the system under study, 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. 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.

The physical, chemical and thermodynamic properties associated with the liquids and liquid mixtures like viscosity, heat capacity, enthalpies of mixing, vapour-liquid equilibria and liquid-liquid equilibria find extensive application in Chemical Engineering design as in most of the chemical process industries, materials are normally handled in fluid form. Since these physical properties 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 present in a mixture can be established from the characteristic abrupt departure from the ideal behaviour of some physical properties, like volume, compressibility, surface tension, viscosity, etc.

The precise knowledge of enthalpies of mixing is important in several chemical engineering applications like in enthalpy balances required for the safe design of distillation columns which often are required to operate at extreme conditions and large capacities. For liquid mixture the assumption of ideal solution may often lead to significant errors. The general tendency is to neglect enthalpies of mixing of solution while designing distillation equipment. In many industrial processes
the heat effects accompanying the change in composition of liquid at constant temperature and pressure may be too small to be of importance. For instance in the distillation of petroleum mixtures, the liquid hydrocarbon phase is close to an ideal solution, rendering the enthalpy of mixing to be negligible in comparison with other heat effects accompanying vaporisation and condensation.

Data on enthalpies of mixing are of practical value in industrial design involving non-ideal liquid mixtures. Tsao and Smith[244] pointed out that this value may run as high as 20,000 cals/mol of solution, which is of the order of heat of reaction in some systems. Excess properties must be determined experimentally for applications where more accurate information is necessary or systems exhibiting greater non-ideality.

The behaviour of the mixture can be easily determined if deviations from ideality are negligible. 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. The deviations of a mixture in terms of properties of mixing, when determined, can be further utilised to understand the molecular behaviour of components and conclusions can be drawn regarding the size, shape and forms existing between the constituent molecules.

In this work enthalpies of mixing are measured for mixture involving C₈ aromatic compound (Xylenes) as one component and esters and acid being the other component. Xylene is a
constituent of aromatic petroleum fraction. Distillation of these higher aromatic fractions to obtain pure components often involve super fractional or azeotropic and extractive processes adding to the cost of purification.

1.2 Scope of Present Work

The present study is a continuation of systematic studies on heats of mixing, densities, viscosities and ultrasonic velocities of binary mixtures involving C_8 hydrocarbons as one of the components.

The main objectives and scope of this work are:

- To determine, experimentally, heats of mixing of binary mixtures involving C_8 hydrocarbons as one of the components.

- To investigate and evaluate the possibility of predicting, accurately, heats of mixing of the systems studied, using different models.

- To evaluate the ASOG interaction parameters, for the group pairs, which have not been reported earlier.

- To determine, experimentally, the densities, ultrasonic velocities and viscosities for the systems whose excess enthalpies have been determined.

- To evaluate the results of the ultrasonic velocity and viscosity determination in the light of molecular interactions between the molecules constituting the mixture.

- To assess the correlations, reported in the literature, in representing the experimental viscosity and ultrasonic data.

- To study the possibility of predicting excess enthalpies of mixing from experimental ultrasonic velocity and viscosity data.