This is a study of vapour - liquid and liquid - liquid equilibria, particularly the latter, of complex fluids. Traditionally, the composition of such fluids are expressed in terms of pseudocomponents despite several known shortcomings. An alternate approach is to use the concept of continuous component - a possibility which does not seem to have been properly exploited. This concept is not a new one but very few studies have been reported in literature. These are mainly confined to V - L - E situations and there has hardly been any application to industrial problems. Investigation of this approach forms the core of this work. Furfural extraction of high boiling petroleum fraction, an important refinery operation, has been analysed and used to illustrate the application of this methodology to L-L-E in particular. The objectives of this work are:

a. Setting up a framework for V-L-E and L-L-E computations, particularly the latter by continuous thermodynamics.

b. Identification of liquid models easily adaptable for representation of complex mixtures as continuous distributions.

c. Application of this methodology specifically to systems containing furfural and heavy petroleum fractions, which occur frequently in lube stock processing in refineries.

In addition to L-L-E, the batch distillation and its inverse problem, both of which have received scant attention, have been analysed. Also, certain amount of experimental data on L-L-E have
been collected and UNIFAC parameters determined. The major results obtained may be stated as follows:

a. A methodology for solving the inverse batch distillation problem has been formulated.

b. The UNIFAC group contribution model has been identified as one of the most suitable models compatible with continuous component representation.

c. L-L-E data for furfural-hydrocarbon and aniline-hydrocarbon systems have been collected. UNIFAC interaction parameters for several groups with their temperature dependence have been determined.

d. Solubilities of hydrocarbons in furfural and the effect of their interaction on the solubilities have been investigated theoretically.

e. Comparison of pseudocomponent and continuous component models for L-L-E of furfural extraction shows that the results of the pseudocomponent method are quite sensitive to the choice of the representative components and may produce widely different results, while no such ambiguities occur for continuous representations.

The thesis has been presented in five chapters with contents as follows:

Chapter I:
The problem and the scope of work have been defined and a literature survey has been made.
Chapter II:
This contains basic theoretical framework for continuous thermodynamics. V-L-E problems have been analysed, particularly the batch distillation and its inverse problems.

Chapter III:
The reasons for choosing UNIFAC model for representing the liquid phase have been put forth. The experimental work and determination of the UNIFAC parameters have been presented.

Chapter IV:
Computational procedure for L-L-E of complex mixtures has been developed and tested. Sulfolane extraction of a kerosene fraction has been treated as an example.

Chapter V:
L-L-E of furfural-hydrocarbon, particularly petroleum fractions have been studied. Extraction of a hypothetical hydrocarbon mixture in the lube stock range by furfural have been investigated and the pseudocomponent and the continuous component methods have been compared.