INTRODUCTION

## 1.1 RECENT APPROACHES TO VLE CALCULATION

Vapor-liquid equilibrium (VLE) relationships are needed in the solution of many engineering problems. They are essential to the design of many kinds of industrial equipment and in the simulation of separation units e.g., distillation, absorption and extraction.

Very broadly, practical methods to predict VLE can be divided into equation of state (EOS) and activity coefficients approaches [1]. The first uses an equation of state to represent both phases, while the second uses an equation of state for the vapor phase and an activity coefficient for the liquid phase.

At low to moderate pressures, the activity coefficient approach has been found to correlate a wide variety of complicated phase behavior [ 2 ]. But at high pressure, including the critical region, the equation of state approach has a number of advantages in comparison with the other approach.

1. At the critical region, where difference of volumetric properties between the two phases vanishes, anomalous results are obtained from the activity approach since different models are

employed for the vapor and liquid phases. While the equation of state approach predicted critical regions quite naturally [3].

2. In high pressure vapor-liquid equalibria, we frequently must deal with supercritical components, that is, the critical temperature of one (or possibly more) of the components are below the system temperature. The activity approach is complicated by the fact that the supercritical components do not exist as pure liquids at the temperature and pressure of the system. Thus one cannot know the fugacity of the pure liquid upon which the activity coefficient is usually based. The equation of state approach avoids the use of activity coefficients and thereby avoids the problem of standard states for supercritical components.

3. Although there are many expressions and procedures available for estimating activity coefficients, but none of them can be applied to calculate activity coefficients from the most widely used properties of pure components such as critical temperature, critical pressure and acentric factor. While the EOS approach allows deriving the properties of mixtures from the knowledge of the behavior of pure components.

4. At high pressure, the usual assumption of pressure independence of the activity coefficient in activity approach is not satisfactory.

Therefore, calculating VLE from an EOS is attractive, however the accuracy of such calculations necessarily depends on the EOS used.

## 1.2 STATEMENT OF THE PROBLEM

It is widely recognised in the Gas-Processing Industry that current methods for calculating VLE of natural-gas mixtures can be unreliable at high pressure. There is a need for a reasonably accurate but simple thermodynamic model for natural-gas mixtures that can be used in a flow-sheeting program. In practice, a cubic EOS is often preferred.

Among the equations of state frequently used in chemical engineering is that proposed by SOAVE(SRK) in 1972 [6]. It is remarkably simple and was not significantly less accurate than other methods [3-5]. Numerous modifications have been proposed in recent years to improve the applicability of the SOAVE equation to the calculation of VLE values. Compilations of these efforts are available in the literature [10,12]. While accuracy is sometimes improved, there is not always a favorable trade obtained in computer time nor certainty for convergence. Their ability to predict VLE were shown to be based on mostly binary data at low temperature. It is not immediately evident that these equations of state are also applicable to high temperature systems containing supercritical compound. This work considers the applicability of some particular equations of state for such mixtures and more tests to be performed on a multicomponent systems.

The calculation of VLE requires a binary interaction coefficients, $K_{ij}$, which should be determined from experimental data. Part of this work is devoted to this evaluation to provide optimal binary interaction coefficients for many systems.

## 1.3 PURPOSE OF THE RESEARCH

1. To do a literature survey in order to select the most prospective equations of state for VLE calculations of natural gas at high pressure.

2. To test the ability of the chosen EOS in predicting VLE and hence the validity of all the correlations associated with the equations of state.

3. To evaluate the parameters in the EOS chosen, if they are not given in the literature

## 1.4 SCOPE OF THE RESEARCH

1. Components included are $CO_2, N_2, C_1$ to $C_{10}$

2. For binary systems

$$T > T_c \text{ of the light component}$$

$$P < P_c \text{ of mixture}$$

For multicomponent systems

$$19 < P < 206 \text{ atm}$$

$$310 < T < 366 \text{ K}$$