CHAPTER 1

INTRODUCTION

For process calculations particularly in petroleum, petrochemical and cryogenic technology, equations of state have proved to be extremely useful. They have proven to be useful tools in industrial applications, allowing prediction of equilibrium phenomena and sizing of process equipment from a relatively small amount of experimental data.

Equations of state are simple and can be solved with a straightforward algebraic procedure , so that the equations lead to robust computer programs for the prediction of thermodynamic data with relatively short computing times. Equations of state contain only a small number of adaptable parameters which can easily be related to the critical properties, so that the equations lend themselves well for generalization and application to mixtures.

Ever since the appearance of the van der Waals equation, many modification have been made in the literature to improve models. One of the most successful one was the two-parameters empirical equation proposed by Redlich and Kwong (1). Since that time, numerous modified Redlich-Kwong (RK) equations have been proposed in recent years to calculate the volumetric properties of pure compounds and of mixtures with a good accuracy and to improve the applicability of the RK equation to the calculation of vapor-liquid equilibrium (VLE). One modified RK

equation by Soave (2) is the Soave-Redlich-Kwong (SRK) equation has gained acceptance by the hydrocarbon processing industry because of the simplicity of the equation itself and its capability for generating resonably accurate equilibrium ratios in VLE calculation. Then, Peng and Robinson (3) proposed the new simple equation which give better results than the SRK equation, the PR equation gave improved liquid density values as well as accurate vapor pressure and equilibrium ratio.

Recently, much attention have been given to the perturbed hard sphere equation of state with consideration of the forces of repulsion between rigid spheres, the repulsive term RT/(V-b) of the RK equation of state is modified. The perturbed hard-sphere equation of state by Carnahan and Starling (4) was found to give good performance for density and enthalpy deviation of pure substance and some hydrocarbon binaries. However, the repulsive term of hard sphere equation of state modified by De Santis et al.(5), Nagata and Yasuda (6) and Nagamura et al.(7) are still too complicated. A simple form of hard sphere repulsive term was adopted by Ishigawa, Chung and Lu (8) ,this hard-sphere equation of state was claimed as somewhat superior to the SRK and PR equation.

The purpose of this work is to modify the hard-sphere equation of state in order to predict accurately the thermodynamic properties (vapor pressure , saturated liquid and vapor volume) of pure component light hydrocarbons. It is expected that this work is capable of widespread applications and yet, can lead to very accurate predictions of VLE calculations.

The scope of this work is as follows :

1. To propose a modified hard sphere equation of state which is the most prospective equation of state for predicting pure component volumetric properties of light hydrocarbons.

2. To evaluate the parameters in the modified hard sphere equation of state which is best fitted to the saturated liquid volume.

3. To test the ability of the modified hard sphere equation of state in predicting pure component volumetric properties of light hydrocarbons and hence the validity of all the correlations associated with the equation of state.