



Chapter One

Introduction

The prediction of thermodynamic properties of mixtures and phase equilibria rests heavily on the use of equations of state for mixtures and liquid phase activity coefficient models. Of late serious consideration is being given to the prediction of phase equilibria using only equations of state for both phases. The predictive power of any equations of state is limited to the availability of the interaction parameters used in combining pure component constants of the equations and the type of mixing rules employed.

Probably the most successful equations of state for phase equilibrium calculations have been those proposed by Soave (1) and Peng-Robinson (2). These equations are the two-parameter equations that have been accepted in their simple form and good accuracy. In the recent years, there has been increased interest in modifying the three-constant cubic equations of state. In 1980, Schmidt and Wenzel (3) first recommended the acentric factor as a third parameter and a similar form was proposed by Harmens and Knapp (4). Patel and Teja (5), in 1982, proposed a different form that used a function of the critical compressibility factor as the third parameter which, in turns, is a function of the acentric factor. These three-parameter equations have

proved to be more accurate in predicting pure substance properties than the original two-parameter equations.

However, to obtain better results with these equations of state, the optimum binary interaction coefficients (K_{ij}) are required in all equations. It is obvious that these coefficients can improve the accuracy of phase equilibria calculations especially for the mixtures containing polar substances such as carbon dioxide.

In this work, the optimum binary interaction coefficients (K_{ij}) were calculated from isothermal experimental vapor-liquid equilibrium data for several carbon dioxide-hydrocarbon, methane-heavier hydrocarbon, and ethane-heavier hydrocarbon mixtures at various temperatures using four equations of state; Patel-Teja, Schmidt-Wenzel, Peng-Robinson, and Soave-Redlich-Kwong equations of state. Two criteria had been used for evaluation of the optimum K_{ij} . They were the minimization of deviation in predicted bubble point pressures criterion and the minimization of the deviation between calculated component vapor and liquid fugacities criterion. Further, the applicability of the optimum K_{ij} values was tested with the PT and SW EOS to predict the bubble point pressures of those mixtures and compared with the results from the SRK, PR EOS, and experimental data.