CHAPTER III

MIXING RULES AND COMPOUND CLASSIFICATION

3.1 <u>MIXING RULE</u>

The equation of state are generally developed for pure fluids first, then extended to mixtures by using mixing rules. The mixing rules are simply used to calculate mixing parameters which are equivalent to those of pure substances.

Most of the simple equation of state evolved from the Van der waals' equation use Van der waals' mixing rule with or without modifications. From the viewpoint of mathamatical expression, the Van der waals' mixing rule are special forms of the second virial coefficient mixing rule:

$$amix = \sum_{i}^{n} \sum_{j}^{n} y_i y_j (a_i a_j)^{0.5} \ (1\text{-}Kij) \qquad (3.1)$$

$$bmix = \sum_{i}^{n} y_i b_i \qquad (3.2)$$

x_i is mole fraction of component i in liquid phase

x_j is mole fraction of component j in liquid phase

y_i is mole fraction of component i in vapor phase

y_j is mole fraction of component j in vapor phase

where amix is energy parameter in mixture

bmix is volume size parameter in mixture

For the Quartic EOS, the following mixing rules are used in this work and four parameters in Quartic EOS are devided in two groups.

1. The volume size parameters : e , β
2. The energy parameters : c , a

Therefore,

$$emix = \sum_{i}^{n} y_i e_i \quad (3.3)$$

$$= y_1 e_1 + y_2 e_2 \quad (3.4)$$

$$\beta mix = \sum_{i}^{n} y_i \beta i \quad (3.5)$$

$$= y_1 \beta 1 + y_2 \beta 2 \quad (3.6)$$

$$amix = \sum_{i}^{n} \sum_{j}^{n} y_i y_j (a_i a_j)^{0.5} (1\text{-}Kij) \quad (3.7)$$

$$= y_1^2 a_1 + 2 y_1 y_2 (a_1 a_2)^{0.5} (1\text{-}Kij) + y_2^2 a_2 \quad (3.8)$$

$$cmix = \sum_{i}^{n} \sum_{j}^{n} y_i y_j (c_i c_j)^{0.5} \quad (3.9)$$

$$= y_1^2 c_1 + 2 y_1 y_2 (c_1 c_2)^{0.5} + y_2^2 c_2 \quad (3.10)$$

Contribution of parameter c to the overall value is very much less than that of parameter a . Therefore , effect of the interaction for parameter c is neglected.

3.2 Compound Classification (Ewell, Harrison and Berg, 1994)

- Classification of molecules is based on potential for forming hydrogen bonds.

Class 1 Molecules capable of forming three-dimensional networks of strong H-bonds

Examples: Water, glycerol, glycols, amino alcohols, hydroxyamines, hydroxyacids, polyphenols, and amides

Class 2 Other molecules containing both active hydrogen atoms and donor atoms (O, N and F)

Examples: Alcohols, acids, phenols, primary and secondary amines, oximes, nitro and nitrile compounds with α- hydrogen atoms, ammonia, hydrazine, hydrogen fluoride, and hydrogen cyanide

Class 3 Molecules containing donor atoms but no active hydrogen

Examples: Ethers, ketones, aldehyde, esters, tertiary amines (including pyridine type), and nitro and nitrile compounds without α-hydrogen atoms

Class 4 Molecules containing active hydrogen atoms but no donor atoms that have two or three chlorine atoms O the same carbon atoms as a hydrogen atoms, or one chlorine on the same carbon atom and one chlorine on the same chlorine atoms on adjecent carbon atoms,

Examples: $CHCl_3$, CH_2Cl_2, CH_3CHCl_2, CH_2ClCH_2Cl, $CH_2ClCHClCH_2Cl$, and $CH_2ClCHCl_2$

Class 5 All other molecules having neither active hydrogen atoms nor donor atoms

Examples: Hydrocarbons, carbon disulfide, sulfides, mercaptans, and halohydrocarbons not in Class 4