CHAPTER II



LITERATURE REVIEW

This chapter consists of two parts. The first part will cover the experimental works on measuring density of some binary and ternary systems by using a vibrating-tube densitometer of Anton Paar; for example Model DMA 60/512. The density data are used to predict many thermodynamic properties such as molar volume, excess molar volume and so on. In the second part, some applications of well-known equations of state are presented.

2.1 Experimental Study on Density of Mixtures

Asfour and Siddique (1990) determined density-composition data for eight binary mixtures, toluene-n-octane, toluene-n-decane, toluene-n-decane, toluene-n-tetradecane, toluene-n-hexadecane, ethylbenzene-n-octane, ethylbenzene-n-tetradecane and ethylbenzene-n-hexadecane at 293.15, 298.15, 308.15, and 313.15 K over the entire composition range with a vibrating-tube densitometer, Anton Paar Model 60 with Model 602 measuring cell. Temperature fluctuations in the density meter were kept within ± 0.01 K with a Haake Model N4-B circulator with a calibrated platinum temperature sensor (IPTS-68). The results that the experimental data were used to calculate excess volumes of mixing. Excess volume of mixing generally increased with increasing chain length of the n-alkane component. This suggests that molecular size is probably a primary factor affecting the excess volume of mixing for the systems investigated.

Chevalier et al. (1990) measured kinetic viscosities and densities of 68 linear, branched, cyclic and aromatic hydrocarbons binary liquid systems, especially the system

benzene and cyclohexane have been determined at 298.15 K over the entire composition range. Liquid densities were measured with a DMA 02D Anton-Paar density meter which was calibrated with octane and decane.

Stefanos and Constantinos (1989) determined experimental dynamic viscosities and densities of the binary and ternary mixtures of benzene, ethanol, and n-heptane in liquid phase at 298.15 K. The densities have been measured in a vibrating-tube densitometer, Anton Paar Model DMA 60/602. Bidistilled water and air were used as calibrating substances. The temperature in the measuring cells was regulated to 25 ± 0.01°C through a Haake ultrathermostat and measured by a precision digital thermometer, Anton Paar Model DT-100. They found that the data are correlated with the generalized corresponding states method of Teja and Rice by treating the ternary system as pseudobinary and by using only binary information.

Lee et al. (1990) measured densities of mixtures of water-methanol, water-ethyleneglycol, methanol-ethylene glycol, and water-methanol-ethylene glycol at 283.15, 293.15, and 303.15 K and at atmospheric pressure. Density measurements were carried out with an Anton Paar DMA 60/512 vibrating-tube densitometer and was calibrated for each temperature with redistilled water and dry air at atmospheric pressure. The measuring cell was thermostated by using a Haake F3 digital circulator, the temperature being controlled within \pm 0.01 K. The analysis showed that the data were used to calculate excess volumes, are all negative over the entire composition range.

Marchetti et al. (1991) determined densities of the binary mixture 1,2-ethandiol-2-methoxyethanol in the whole composition range at 19 temperatures between 263.15 and 353.15 K and at atmospheric pressure by using a digital density meter(Anton Paar DMA 60) equipped with a density-measuring cell (DMA 602). The instrument was calibrated with bidistilled water and dried air at each investigated temperature. The

temperature was maintained constant to \pm 0.02 °C by means of two Lauda K2R thermostatic baths in cascade. The thermal control was checked by a thermo resistance Pt100 (Tersid, Milan) inserted into the jacket of the measuring cell and near the sample capillary tube. The results showed that the excess molar volumes calculated from the density values are negative at all concentrations and become more negative with increasing temperature.

Ormanoudis et al. (1991) measured densities for the binary mixtures n-hexane-ethanol and n-hexane-1-propanol in liquid phase at the pressure range from 1 to 340 bar and the temperature of 298.15 K. At atmospheric pressure the densities have been measured in a vibrating-tube densitometer, Model DMA 60/602 of Anton Paar. At higher pressures, a high pressure density cell was used that consist of a high-pressure density cell, Model DMA 512 of Anton Paar. Bidistilled water and air were used as calibrating substances. The temperature in the measuring cells was regulated through a Haake ultrathermostat and was kept constant to within 0.01 K, as measured by a precision digital thermometer, Model S1220 of Systemteknik. They found that at the constant temperature, the pressure increases as the density increases. Moreover, the data have been for calculating excess volume, isothermal compressibility, and thermal expansion coefficients.

Dimitri et al. (1991) measured densities and viscosities of the quaternary system benzene, cyclohexane, ethanol and n-heptane and its constituent binaries at temperature 298.15 K with a vibrating-tube densitometer, Model DMA 60/602 of Anton Paar. Bidistilled water and air were used as calibrating substances. The temperature in the measuring cells was regulated to $25.00 \pm 0.01^{\circ}$ C through a Haake ultrathermostat and was kept constant to within 0.01 K, as measured by a precision digital thermometer, Model S1220 of Systemteknik with a specially designed sensor. The results

showed that these data used for testing the predictive character of the generalized corresponding states (GCS) model of Teja and Rice.

Wei and Rowloy (1984) measured densities at 298.15 K and ambient pressure for 20 ternary systems with calculation digital densitymeter (Anton Paar, Model DMA45). These systems were chosen to represent different types of interactions, including polar-polar, polar-nonpolar and nonpolar-nonpolar. The density cell was water jacketed and maintained isothermal to \pm 0.002 K by circulating water from a Tomson 45-L visibility bath. Air and distilled, deionized water were used as reference fluids to calibrate the densitometer.

2.2 Study of Equations of State

Chang et al. (1983) used the Soave modification of the Redlich-Kwong equation of state to predict phase equilibrium in mixtures found in acid gas removal processes used to clean gases produced from coal. They studied binary interaction parameters in Soave equation that were estimated from available equilibrium data by using the Fibonacci search technique to determined optimum parameters. The results showed that the interaction parameter in the methanol-nitrogen system is a strong function of temperature. The interaction parameters for methanol-carbon dioxide and methanol-carbonyl sulfide mixtures are weak functions of temperature. Interaction parameters for the other methanol-gas and gas-gas mixtures in this work were assumed to be independent of temperature. Hence, introduction of a binary interaction parameter in the Soave equation makes it possible to calculate phase equilibrium behavior for nonhydrocarbon mixtures.

Djordjevic et al. (1994) examined the effects of the sample composition-dependent combining rules such as conventional one binary parameter, Adachi-Sugie-type two binary parameter (AS) and van Laar-Stryjek-Vera-type two binary parameter (VLSV)

and Huron-Vidal_NRTL mixing rules and four well known equations of state: the Redlich-Kwong (RK), the Soave-Redlich-Kwong (SRK), the Peng-Robinson (PR), and the Peng-Robinson-Stryjek-Vera (PRSV) on excess molar volume correlation of toluene and cyclohexane mixtures with n-alkanes. They found that the calculated excess molar volumes are sensitive to the type of cubic EOS used, particularly when the EOS were coupled with the conventional one binary parameter rule. The results with the SRK equation are better than with the RK EOS, while those with the PRSV are better than the results with the PR EOS. Moreover, the HV-NRTL mixing rules coupled with the cubic EOS give a better correlation of V^E for the asymmetric mixtures than in the case when one or two composition-dependent combining rules are couples with the same type of cubic EOS. Furthermore, the PRSV-HV-NRTL has been shown to be the best.

Serbanovic and Djordjevic (1987) investigated the influences of the optimized temperature-dependent interaction parameter of the Soave equation of state on vapor-liquid equilibrium (VLE) calculations of supercritical methane with propane, n-butane and n-pentane. The predicted pressures and vapor mole fractions for each data point were iteratively evaluated through a bubble point calculation from the known values of temperature and liquid mole fractions by using for both phases of the Soave equation. The fibonacci search technique was used to obtain the optimum k_{ij} . They showed that conclusions quoted in early works, interaction parameter is treated as zero or constant value, are not right. In all case, VLE predictions at high temperatures, where methane is the supercritical component, must be performed with the temperature-dependent interaction parameter.