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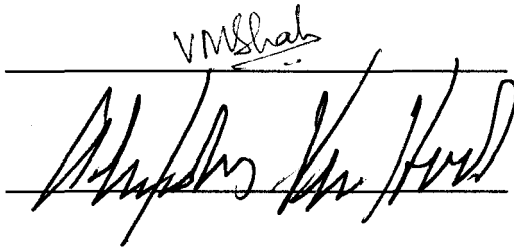


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**APPLICATION OF
A GENERALIZED QUARTIC EQUATION OF STATE
TO PURE POLAR FLUIDS**

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Yen-liang Lin

August 1994

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DEDICATION

This thesis is dedicated to my parents

Mr. Tien-Ken Lin

and

Mrs. Mei-Mi Chou Lin

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In the course of my thesis work, a number of people have assisted me generously. In particular, I am grateful to Dr. Paul Bienkowski, Dr. Hank Cochran, and Dr. Vinod Shah. With their guidance, assistance, criticism, and encouragement, I was able to accomplish this graduate work successfully. I would also like to thank the use of computing facilities at the Oak Ridge National Laboratory. With these offers, this research was proceeded smoothly. My thanks also goes to Dr. Van Hook who served as my committee member for providing me useful advice. Finally, I would like to thank Sanjay Nogaja and my group members, especially; Andrew Champagne. Their assistance and encouragement also helped me with completing this thesis.

ABSTRACT

A generalized four-parameter quartic equation of state proposed by Shah (1992) has been extended to polar fluids. For the use the new generalized quartic equation of state for polar fluids, only four characteristic properties of the pure compound are required, critical temperature, critical volume, acentric factor, and dipole moment. For nonpolar fluids, the previous equation (Shah, 1992) is recovered and its superior performance with nonpolar fluids is retained.

A new set of coefficients for polar fluids in the quartic equation of state has been obtained from multiproperty regressions using various physical and thermodynamic experimental literature data for 30 pure compounds. These regressed coefficients have been generalized and are functions of the acentric factor and the first dipole moment of the fluid. The ability of this equation of state, with the new set of regressed coefficients, to predict physical and thermodynamic properties of pure polar compounds is demonstrated. Those properties predicted include vapor pressure, density, residual enthalpy, enthalpy of vaporization, and second virial coefficient. The capability and accuracy of this quartic equation of state are also compared with the well-known Peng-Robinson equation of state. Especially in the supercritical and compressed liquid region, the new quartic equation of state predicts more accurately than the Peng-Robinson equation of state.

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NOMENCLATURE

a	parameter of the quartic equation of state, MPa / dm^6
b	van der Waals volume, mol / dm^3
B_v	second virial coefficient, cm^3 / mol
c	parameter of the quartic equation of state, MPa / dm^6
e	parameter of the quartic equation of state, mol / dm^3
f	fugacity, MPa
H_r	residual enthalpy, J / mol
H_v	enthalpy of vaporization, J / mol
k_0, k_1	quartic equation of state constants
N	number of data points
P	pressure, MPa
R	universal gas constant, $0.008314 \text{ MPa} \cdot dm^3 / mol \cdot K$
T	temperature, K
V	molar volume, dm^3 / mol
X_i	quartic equation of state regressed coefficients
Z	compressibility factor of a compound

$\alpha(T_r)$ temperature dependence of parameter a

β hard core volume, dm^3 / mol

ρ density, mol / dm^3

μ dipole moment, *debyes*

ω acentric factor

$\xi(T_r)$ temperature dependence of parameter c

Superscripts

calc calculated value

exp experimental value

*** reduced variable

(') liquid at saturation

(") gas at saturation

Subscripts

c value at the critical temperature or the critic point

g gas, single phase region

hs hard-sphere

l liquid phase

v	vapor phase
r	reduced property or constant
s	saturated, two-phase envelope
sl	saturated liquid phase
sv	saturated vapor phase

CHAPTER 1

INTRODUCTION

1.1 An Equation of State

The equation of state (EOS) is the mathematical relationship that relates pressure as a function of temperature and molar or specific volume for any pure fluid, as shown below.

$$P = f(V, T) \tag{1.1}$$

where

P is pressure of the phase,

V is molar volume of the phase, and

T is temperature of the phase.

The EOS is useful not only for predicting values of pressure, temperature, and density, but also for evaluating derived thermodynamic properties. Therefore, the EOS is used to predict fluid phase equilibria and to calculate various thermodynamic and physical properties of pure substances and mixtures, including the following:

1. vapor pressure;
2. density of vapor and liquid phases;

3. pressure-volume-temperature relations;
4. thermal properties (e.g., enthalpy departure, enthalpies of vaporization);
5. second virial coefficient; and
6. phase equilibrium properties of mixtures.

The most commonly used EOSs are cubic equations which have at least two parameters. Cubic EOSs, such as the Redlich-Kwong (Redlich and Kwong, 1949), Soave-Redlich-Kwong (Soave, 1972), and Peng-Robinson (Peng and Robinson, 1976), which are explicit in pressure and of the third degree in volume, are among the most successful of the simpler forms. These equations are composed of two terms: one term models the repulsive forces and the other the attractive forces. Similarly, the EOSs that are explicit in pressure and of the fourth degree in volume are called quartic EOSs. The complexity of these equations and the number of empirical constants depends on the accuracy of experimental measurements, the precision needed, and the experimental range of variables.

Although many useful results of limited range have been obtained, most equations of state are not, in general, effectively applicable to various physical and thermodynamic properties of pure polar compounds. To overcome the limitations of the EOSs, many researchers still continue to develop an EOS to predict more accurately the various thermodynamic properties of fluids over a wide range of states.

1.2 Applications of Equations of State

The contributions of EOSs have been beneficial to the chemical and petroleum industries, particularly in process design and simulation analysis. The development of an EOS for pure fluids is the foundation for future application to mixtures. An EOS that works well for both nonpolar and polar fluids should result in a good prediction of similar or dissimilar mixtures. Obtaining phase equilibrium information for various mixtures over a wide range of temperatures and pressures is of great importance because in chemical plants, separation systems such as distillation or extraction towers play an important role. However, these separation systems are limited by the thermodynamic equilibrium properties of the phase concerned. Therefore, EOSs that are based only on pure compounds and binary mixtures have become a valuable tool for the chemical engineers to model and evaluate fluid phase equilibrium and to conduct in economic evaluations. However, these EOSs predict with different levels of accuracy while evaluating various thermodynamic and physical properties.

Because methods for the description of thermodynamic properties and phase equilibria of fluids are of interest in science, EOSs that are widely used in the chemical industry are needed in chemical engineering. Most EOSs are applicable to hydrocarbons and slightly polar compounds. These equations are broadly developed

for the calculation of thermodynamic properties of nonpolar substances and their mixtures, but are not highly developed for polar fluids such as alcohols, ethers, esters, ketones, refrigerants, etc., because of their poor performance when applied to the latter group of substances.

Recently, a number of researches have been done with the purpose of extending EOSs to polar substances. All of these efforts have introduced an additional parameter that significantly improved the fit of the equation for predicting vapor pressure for polar compounds. However, the resulting correlation, developed by Soave (1972), replaced the acentric factor with two empirical parameters lacking physical meaning. Although Won and Walker (1979) introduced a polar parameter determined by fitting experimental data, the magnitude of this parameter had no correlation to the polarity of the fluid and was negative for some polar compounds (Mathias, 1983). Relatively little work has been reported on the EOS for those fluids whose molecules possess an appreciable dipole moment. For practical applications to systems containing polar fluids, it has become common practice to use empirical extensions of methods originally developed for nonpolar fluids.

1.3 Equations of State for Polar Fluids

The development of EOSs for polar fluids can be divided into two methods: one is developed by an empirical algebraic expression,

and the other through the rigorous statistical mechanical investigation of polar fluids. An extension of an EOS developed for nonpolar fluids to polar fluids often involves using an empirical temperature-dependent parameter in the equation or employing the perturbation theory. The perturbation theory usually leads to separating the parameters of the EOS into the nonpolarity and polarity contributions.

For a nonpolar molecule, the value of the dipole moment is zero because the centers of negative charges and positive charges are identical. However, for a polar fluid, the dipole moment results when the centers of negative charges and positive charges are not coincident. Polarity is defined as the magnitude of a dipole moment expressed in debye units. Roughly, symmetrical molecules have zero dipole moments; however, the molecules with dipole moments greater than 1.0 debye are classified as polar. Therefore, there are additional contributions to pair-potential energies from the polarization or the electrostatic energies associated with dipole, quadrupole, or higher electric moments.

1.4 Motivation

Shah (1992) and Shah et al. (1994) have developed a generalized four-parameter quartic EOS and has applied it to nonpolar fluids. The main objective of the present research is to modify the correlation equations of the parameters a and c in order

to develop a method for extending this EOS to polar fluids using a polar parameter that is numerically related to actual molecular properties such as dipole, quadrupole, and octupole moments and to generate a new set of the regressed coefficients for nonpolar and polar fluids.

The proposed modification implies that the generalized quartic EOS can be extended to polar fluids by adding the fourth characteristic property of the fluid. This further implies that the properties of a polar fluid are equivalent to those of a nonpolar fluid after the incorporation of an additional polar factor. Hence, the dipole moment will be a primary focus in this study. The equation parameters a and c will be made functions of the acentric factor and the dipole moment. Regressions with a database consisting of 30 pure polar fluids will be used to determine the dependence of a and c on the dipole moment and to generate a new set of regressed coefficients for pure polar and nonpolar fluids. To test the capability of the new EOS, the new set of coefficients obtained will be used to predict the properties of some polar compounds that are not included in 30 polar fluids used during regressions. Finally, a comparison of thermodynamic and physical properties calculated by the model quartic EOS with those calculated by the Peng-Robinson EOS will be demonstrated.

CHAPTER 2

LITERATURE REVIEW

The purpose of this chapter is primarily to describe the background on various equations of state, such as the cubic, hard-sphere, perturbed hard-sphere, and other equations of state, and to illustrate the application of these EOSs to nonpolar and polar fluids.

2.1 Cubic Equations of State

Much attention on cubic EOSs has been received in the natural gas and chemical industries since the first practical equation of state was introduced by van der Waals (Rowlinson, 1988) in 1873. The equation proposed by van der Waals (vdW) is the simplest example of a two-parameter EOS that is cubic in volume. It can be written by

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} \quad (2.1)$$

where

R is the universal gas constant,

a is a parameter of measuring the intermolecular attractive force, and

b is a parameter of measuring the excluded volume of the molecules.

The first and second terms of the right-hand side are the repulsive pressure term and attractive pressure term, respectively. When the cubic equation of state is expressed in terms of the volume or compressibility factor, there are three real roots, the largest one is that of vapor, the smallest one is that of liquid, and the intermediate one is without physical significance. Algorithms to solve for roots of cubic equations of state have been reported by Asselineau (1979), Poling et al. (1981), and Gosset et al. (1986). A graphical representation of roots of cubic equations can be seen in Figure 2.1.

After the vdW equation was used for several decades, Redlich and Kwong (1949) modified the attractive pressure term of the vdW equation of state. The Redlich-Kwong (RK) EOS was widely popular and was used in the place of the vdW equation in industry; it can be expressed by

$$P = \frac{RT}{V - b} - \frac{a}{\sqrt{T}(V + b)V} \quad (2.2)$$

To give a good representation in the calculated thermodynamic properties of the fluid, Soave (1972) replaced the temperature-dependent term $a / \sqrt{T}$ of the RK EOS with a function $a(T, \omega)$ involving the temperature and the acentric factor (ω). Thus, Equation (2.2) can be rewritten as

$$P = \frac{RT}{V - b} - \frac{a(T, \omega)}{(V + b)V} \quad (2.3)$$

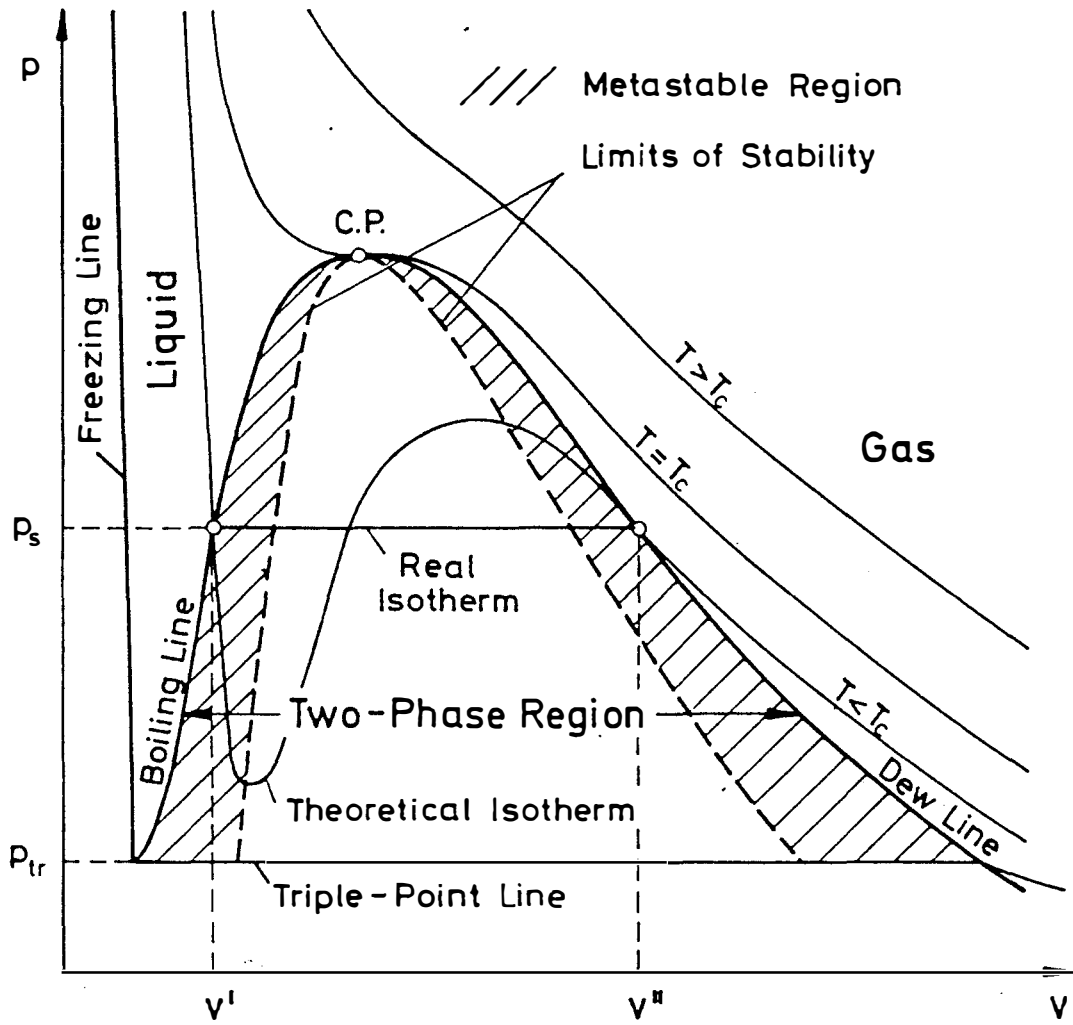


Figure 2.1: A P - V diagram of a pure fluid

However, the Redlich-Kwong-Soave (RKS) equation was found to perform poorly for polar fluids. Gibbons et al. (1984) reported that the modification of the RKS could accurately predict the vapor pressure curve using two parameters from the triple point to the critical point but couldn't accurately predict the critical volume and liquid densities for polar substances. Peng and Robinson (1976) proposed an EOS that is able to more accurately predict the vapor pressure, liquid density, and equilibrium ratios than the RKS equation. The Peng-Robinson (PR) EOS is given as follows:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \quad (2.4)$$

where

$$a = 0.45724 \frac{R^2 T_c^2 \alpha(T_r, \omega)}{P_c}$$

$$\alpha(T_r, \omega) = \left(1 + k(1 - T_r^{0.5})\right)^2$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

These equations contain two parameters, a and b , which are determined by the critical-point conditions, as shown below:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c, P_c} = 0 \quad (2.5)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c, P_c} = 0 \quad (2.6)$$

For polar fluids such as water, ammonia, and others, further modifications were made by Soave (1979) to extend the RKS equation to the calculations of vapor-liquid equilibrium. Sandarusi et al. (1986) presented a four-parameter extension of the RKS equation for modeling the vapor pressure of polar fluids.

Stryjek and Vera (1986) modified the temperature and acentric factor dependence of the attractive pressure term of the PR EOS. The equation developed offers a good reproduction of the vapor pressure for nonpolar and polar compounds. Won and Walker (1979) introduced a polar contribution term into the attractive pressure term of the RKS equation and applied the modified equation to polar compounds; the results were in good agreement with experimental data for the thermodynamic properties of polar gases. However, for the two-parameter equations, the greatest errors are often produced in the critical region because a fixed value of the critical compressibility factor is used for each compound.

To overcome the shortcomings created by not considering the dependence of the critical compressibility factor for each compound, Fuller (1976) and Freze and Chevalier (1978) have employed the third temperature-dependent parameter in the previous equations to emphasize the substance-dependent critical compressibility factor to cause the liquid density and the critical volume to be reproduced accurately for nonpolar substances. Usdin and McAuliffe (1976) used the critical compressibility factor as the fourth property of the

fluid to fit liquid density for nonpolar compounds. A modification of the vdW equation for only nonpolar fluids, introducing the substance-dependent critical compressibility factor, was made by Schmidt and Wenzel (1980). Heyen (1981) and Harmens and Knapp (1980) also proposed a three-parameter cubic equation to offer a good representation of the critical isotherm region.

Patel and Teja (1982) improved the RKS, PR, and Schmidt and Wenzel equations, and the proposed equation, the PT equation, gave good predictions of the liquid volumetric properties and could be applied to some polar fluids. Bazua (1983) and Yu, Adachi, and Lu (1986) developed a three-parameter cubic EOS with one parameter being temperature dependent (3P1T). Yu, Lu, and Iwai (1987) used the 3P1T equation to make simultaneous calculations of vapor-liquid equilibrium and saturated liquid and vapor volumes for polar fluids, which are generally not very reliable. To yield reasonable values of saturation properties for pure fluids, Iwai et al. (1988) applied the capability of the 3P1T equation to polar fluids.

Martin (1979) developed a volume-translation method to improve the prediction of saturated liquid density for pure fluids. Martin (1979) and Abbott (1979) discussed the merits and the limitations of simple cubic equations. A modification of the Martin equation was made by Kubic (1982). Vidal (1983) reviewed a number of three-parameter cubic EOSs and reported that the third parameter generally results in improved liquid density predictions.

Georgeton et al. (1986) presented the comparisons of the capabilities of two- and three-parameter cubic EOSs that are applied to polar fluids.

Adachi (1983) reported a four-parameter EOS in 1983. Trebble and Bishnoi (1987) presented a new four-parameter cubic EOS for polar and nonpolar fluids and described the b covolume parameter, which was mentioned by Heyen (1981) and Watson et al. (1986), as being temperature dependent. Trebble and Bishnoi (1986) compared the pressure-volume-temperature (PVT) of nonpolar and polar fluids from 10 cubic EOSs using 75 pure compounds. Hnedkovsky and Cibulka (1990) analyzed the dependence of the covolume parameter on temperature in cubic equations illustrating the compressed liquid region.

Yarborough (1979), Panagiotopoulos and Kumar (1985), and Morris and Turek (1986) suggested that the use of extended temperature-dependent parameters of the equation, the parameters a and b , allowed a better calculation of both vapor pressure and liquid density. Cisternas (1988) presented a generalized method, an extension technique proposed by Panagiotopoulos and Kumar, to calculate the pure fluid parameters for three-parameter cubic EOS using the Usdin-McAuliffe equation.

However, to avoid the prediction of negative heat capacities, Salim and Trebble (1991) modified the Trebble-Bishnoi equation,

letting the covolume parameter be temperature independent, to perform thermodynamic property consistency. Thus, the predictions of the saturated liquid densities for polar fluids using the previous equations are not very accurately. An improvement can be achieved if the covolume parameter is temperature dependent. However, some weak points appeared, such as a shift of errors to the predictions of saturated vapor densities investigated by Yu et al. (1986) and a thermodynamic property inconsistency in the compressed liquid and the supercritical region proposed by Trebble and Bishnoi (1986), Hnedkovsky and Cibulka (1990), and Salim and Trebble (1991).

A five-parameter cubic EOS was proposed by Kumar and Starling (1982) and Adachi et al. (1986) to present the volumetric properties of the pure fluid. Valderrama and Cisternas (1986), following the studies of Patel and Teja (1982), replaced the acentric factor with the critical compressibility factor in the proposed equation for predicting PVT behavior of polar fluids. However, Valderrama (1990) found that the properties of the fluid using the PT equation in terms of the critical compressibility were not generally valid. Thus, a new generalized correlation, combining the acentric factor and the critical compressibility developed by Valderrama, is used in the PT equation for polar and nonpolar fluids and their mixtures. Yesavage (1986) extended the RKS equation to polar fluids considering the effects of polarity and hydrogen bonding.

Joffe (1987) applied the Martin equation to polar compounds at high pressures using the principle of volume translation as described by Peneloux et al. (1982). Using the volume-translation method, Mathias et al. (1989) proposed a density correction term for the PR EOS and obtained significantly improved predictions of the saturated liquid density.

To account for accurate vapor pressure predictions for polar fluids, Melhem et al. (1989) developed a two-parameter temperature-dependency model which was proposed for the PR equation. Salerno et al. (1986) created a database that was used to develop the vdW-711 equation by Watson et al. (1986). Androulakis et al. (1989) modified the vdW-711 equation to calculate various thermodynamic properties of nonpolar and polar fluids. The predictions for saturation are presented from the triple point to the critical point; however, poor results for the PVT behavior appear at intermediate reduced temperatures.

Considering the properties of pure polar fluids, Halm and Stiel (1967) introduced a polar factor to predict the vapor pressure and entropy of vaporization for polar compounds. Bender (1973) developed an equation that provides a reliable correlation for pure fluids. To evaluate accurately the thermodynamic properties of nonpolar and polar fluids over an extensive range of density and temperature, Platzer and Maurer (1989) used the critical temperature, the critical density, the acentric factor, and a polar

factor developed by Halm and Stiel (1967) to extend the Bender EOS. Twu et al. (1992) proposed an optimum three-parameter cubic EOS to improve the capability of two-parameter and three-parameter equations of state in liquid density and vapor-liquid equilibria calculations.

So far, most cubic EOSs that have been proposed have included the vdW's excluded volume expression for the repulsive pressure, which is not qualitatively effective for dense fluids. A major limitation in their use has been their restricted application to weakly polar compounds. Although cubic EOSs have substantial limitations and cannot represent simultaneously all thermodynamic functions, their simplicity and practical success in predicting phase equilibria continue to stimulate further developments.

2.2 Other Equations of State

The development of an equation for providing a more accurate description of the thermodynamic properties of pure fluids and their mixtures is needed in supercritical fluid extraction. Thus, simple cubic EOSs have been rendered complicated by many authors to compensate for the weak points of cubic equations.

Barker and Henderson (1967) and Weeks et al. (1971) made great progress in presenting a semiempirical EOS based on the statistical mechanical perturbation theory. The perturbation theory

of Barker and Henderson was applied to polar fluids by Masuoka et al. (1977). Subsequently, a more practically oriented, generalized vdW theory that was developed to rationalize EOSs was proposed by Vera and Prausnitz (1972), Sandler (1985), Lee et al. (1985), and Abbott and Prausnitz (1987). Yokoyama et al. (1983) used the concept of perturbation theory to develop a semiempirical equation for polar fluids. Yao et al. (1982) used the Monte Carlo method to simulate the dipolar interaction. Masuka and Chao (1984) proposed a dipolar pressure equation from the results of Yao et al. and used it to expand the chain-of-rotators equation of Chien et al. (1983) to form an equation for polar fluids. Kanchanakpan (1984) utilized the theories of statistical mechanics to develop an equation for pure nonpolar and polar fluids.

Kubic (1986) proposed an empirical quartic EOS, which is based on the simple hard-chain model, by simplifying the Beret-Prausnitz generalized vdW partition function. For the repulsive term he used the approximate hard-core equation as developed for the cubic chain-of-rotators (CCOR) equation, and he also extended the proposed equation to polymer mixtures. To overcome the shortcomings of cubic EOSs including the vdW repulsive pressure term for dense fluids, Carnahan and Starling (1969) developed the compressibility factor of the hard-sphere EOS based on the analysis of the reduced virial series. Obviously, if the hard-sphere equation is to serve as a basis in the study of real fluids, an accurate and simple expression is needed. The Carnahan-Starling equation (C-S) is one of the most

accurate hard-sphere equations and retains a significant degree of simplicity.

However, the C-S equation makes the solution of the EOS and analytical manipulation more difficult because of its analytical complexity. Without using the C-S equation as the repulsive term, Soave (1990) extended the excluded volume term of the vdW form to develop a quartic equation of state for PVT and vapor-liquid equilibrium calculations for pure nonpolar and polar compounds.

Hall (1972) proposed another hard-sphere equation which agreed with the molecular dynamics data of Alder et al. Tsonopoulos and Heidman (1985) reported that it has little influence on practical calculation even if the difference between the vdW and C-S repulsive terms is quite large. The EOS including a hard-core repulsive term and a simple attractive term was investigated by Anderson and Prausnitz (1980) and Dimitrelis and Prausnitz (1986).

Pults et al. (1989) proposed a chain-of-rotators group contribution (CORGC) EOS for the predictions of phase equilibrium and volumetric properties of nonpolar fluids and their mixtures. Shariat et al. (1993) obtained the revised parameters for the CORGC equation and applied it to evaluate thermodynamic properties of nonpolar and polar fluids; moreover, the predicted values of vapor pressure, saturation volumes, and heat of vaporization are better than those obtained by Pults et al. (1989). Zia-Razzaz and

Moshfeghian (1993) also used the CORGC equation to predict thermodynamic properties of polar and nonpolar fluid mixtures by means of a new mixing rule.

An EOS for polar and nonpolar fluids, based on the dipolar hard-sphere theory proposed by Rushbrooke et al. (1973) and the computer simulation data for n-butane (Vimalchand and Donohue, 1989), is reported by Brandani et al. (1992). They made a comparison of this equation with the Soave cubic EOS for polar fluids. This equation was also extended to mixtures by Brandani et al. (1994).

A four-parameter CCOR EOS based on the perturbation theory was developed by Lin, Kim, Guo, and Chao (1983). The CCOR equation is a modification of the chain-of-rotators equation of Chien et al. (1983), which is developed by means of a partition function of the rotational motion of polyatomic molecules. Guo et al. (1985) investigated the vapor pressure of polar fluids with the CCOR equation and extended it to mixtures.

However, at low reduced temperatures the CCOR equation that was investigated by Trebble and Bishnoi (1986) failed to evaluate ammonia PVT behavior. Kim et al. (1986) presented the CCOR equation for nonpolar fluids and mixtures. Leet et al. (1986) retested the ability of the CCOR to predict the vapor pressure and liquid density of polar compounds by replacing the acentric factor

with the critical compressibility factor as the third property of the fluid. To improve the overall capabilities of the CCOR, Ciric and Paunovic (1994) adjusted the equation parameters that accurately produce the saturated and supercritical vapor densities and subcooled liquid densities at lower pressures and temperatures.

2.3 Perturbed Hard-Sphere Equations of State

To obtain a more accurate EOS, several authors used expressions for the attractive contribution obtained by fitting a proper power series to computer simulation data. Alder et al. (1972) proposed the attractive term for the fluid based on the molecular dynamic studies of a square-well fluid. Chen and Kreglewski (1977) proposed a more complex perturbation equation by incorporating Boublik's hard convex body equation for the repulsive pressure term and Alder et al.'s polynomial for the attractive pressure term into the Boublik-Alder-Chen-Kreglewski (BACK) EOS. The BACK equation was also further studied by Simnick et al. (1979) and Machat and Boublik (1985). Lee and Chao (1988) developed an EOS for polar fluids by modifying the BACK equation with a polar pressure derived from the studies of water.

Perturbed hard-sphere EOSs are a comparatively recent and highly promising development, and work is continuing in this area. Several studies based on perturbed hard-sphere EOSs have been proposed. Carahan and Starling used the C-S equation as the

repulsive term and adopted the attractive term of the vdW and RK EOSs, respectively. The modified RK equation gives superior performance for densities and enthalpy predictions of pure fluids. The Perturbed Hard-Chain Theory (PHCT), which was proposed by Beret and Prausnitz (1975), is utilized by means of the C-S equation and Alder et al. expressions to form a three-parameter equation for molecules treated as chains of segments. Gmehling et al. (1979) extended the PHCT to polar fluids.

Bienkowski et al. (1973) proposed a generalized hard-sphere equation in which the C-S equation was used, with the attractive terms being expressed by a truncated virial expansion. Boublik and Nezbeda (1977) developed a general equation of nonspherical hard convex bodies that reduces to the C-S equation if the nonspherical parameter of hard convex body is equal to the value of 1. De Santis (1976) adopted the Clausius attraction term and the C-S equation to obtain an equation of state with two temperature-dependent parameters.

Nakamura et al. (1976) developed a mathematically simple perturbed hard-sphere equation for nonpolar and polar fluids. Siddiqi and Lucas (1989) combined the features of the PHCT and the BACK equation and extended the resulting EOS to polar molecules. A perturbed hard-sphere EOS for polar and nonpolar fluids, based on the C-S equation, with an empirical attractive term was proposed by Mulia and Yesavage (1989). The resulting equation accurately

predicts vapor pressures of nonpolar and polar fluids and is suitable for calculating the heat of vaporization of pure fluids.

To describe properties of polar fluids, the perturbation theories are developed using a reference system that represents the repulsive pressure term. The typical reference systems are combinations of hard-sphere or hard-convex bodies. However, for highly polar fluids, these reference systems can result in difficulties in convergence of the perturbation series. Chung et al. (1984) reported that a more complicated reference system is needed to overcome this obstruction. For the dipolar hard-sphere fluids, Bryan and Prausnitz (1987) presented a reference system with the same dependence on density as that given by the C-S equation, but the coefficients are expressed as functions of temperature through the series of reduced dipole moment. Thus, the proposed equation combines the reference system with a semiempirical perturbation term to represent thermodynamic properties of pure polar fluids.

Dohrn and Prausnitz (1990) presented a simple but reasonable perturbation term for the C-S hard-sphere reference equation to test nonpolar fluids and made a comparison of the proposed equation with seven other two-parameter equations. The results obtained by Dohrn and Prausnitz illustrate that a perturbed hard-sphere EOS cannot accurately represent the properties of a real fluid over a wide range of temperatures and densities if the volume parameter is not dependent on density and temperature.

Shah (1992) developed a four-parameter perturbed hard-sphere EOS which is a generalized quartic EOS, by combining the repulsive term, by means of a fitting of the molecular dynamics data of Alder et al., with an empirical attractive term. Shah reported that one root of this equation has no physical significance because it is always less than the close packed volume of the fluid and the behavior of the remaining three roots are equal to that of the three roots of a cubic EOS. Thus, the resulting equation possesses the advantages of the cubic EOS, existence of analytical solutions and unequivocal identification of roots. With its simplicity and accuracy, the resulting equation only requires three properties of nonpolar fluids: the critical temperature, the critical volume, and the acentric factor; moreover, it marks a significant improvement over the PR equation in the supercritical and compressed liquid region.

Thus, in general, cubic EOSs have been widely used by the chemical industries and researchers due to their simplicity and practical success in calculating phase equilibria. However, the representation by cubic EOSs of various thermodynamic properties with desired accuracy is not entirely reliable. It would be desirable to develop a new generalized EOS which retains the advantages of cubic EOSs while significantly reducing their disadvantages. Hence, a generalized quartic EOS was proposed by Shah which generally outperforms cubic EOSs for nonpolar fluids. Extension of Shah's equation to polar fluids is accomplished in this work.

CHAPTER 3

DEVELOPMENT OF A GENERALIZED QUARTIC EQUATION OF STATE FOR POLAR FLUIDS

This chapter is intended to present the theory of the generalized quartic EOS, to (1) set up some parameter equations that are suitable for polar fluids, (2) evaluate some thermodynamic properties of the polar fluid for the quartic EOS, and (3) provide two mathematical algorithms for estimating the regressed coefficients of parameter equations in the generalized quartic EOS.

3.1 The Generalized Quartic Equation of State

The generalized four-parameter quartic EOS (Shah, 1992) has solved some problems encountered with conventional cubic EOSs. Like the van der Waals and Peng-Robinson EOSs, this quartic EOS also characterizes pressure as the sum of two terms, the repulsive term and an empirical attractive term. Most traditional cubic equations of state used the repulsive term in the vdW hard-sphere equation as their repulsion pressure terms. The repulsive term in the vdW equation states that the covolume parameter b is four times the hard-sphere volume of molecule. However, this hypothesis resulted in larger prediction errors by those equations of state while considering the repulsive force at higher densities. Thus, the

repulsive pressure term is not appropriate when the EOS is used for dense fluids.

Unlike the previous EOSs, the repulsive pressure of Shah's quartic EOS describes the molecular dynamics results of hard spheres. Shah (1992) adopted a mathematically simple repulsive term as the repulsive force of the hard spheres in the generalized quartic EOS. This term is a new fitting of computer-simulated results of the hard spheres (Alder and Wainwright, 1960), as given below:

$$P_{rep} = \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} \quad (3.1)$$

where

β is the hard-sphere molar volume of the compound, and the values of k_0 and k_1 ,

$k_0 = 1.2864$, and

$k_1 = 2.8225$ were obtained using regressions.

The attractive pressure term modeled in the previous equations of state was not applied to Shah's quartic EOS. Nor did Shah use the complicated series expansion in molar volume, the other attractive pressure term which has been derived in the perturbation theories. Instead, a simple functional form was considered for the development of the attractive pressure term in the quartic equation of state. Thus, Shah (1992) proposed an approach to find the attractive pressure term, which was

accomplished by taking the real fluid data for argon and hard-sphere compressibilities calculated from Equation (3.1). This term is an empirical fitting that was obtained by plotting Z_{att} versus the reduced density at different reduced temperatures. Z_{att} is defined as the difference between the experimental compressibility (Z_{exp}) and the hard-sphere contribution to the compressibility (Z_{hs}). Z_{hs} is obtained by Equation (3.1) and is given by:

$$Z_{hs} = \frac{V}{(V - k_0\beta)} + \frac{\beta k_1 V}{(V - k_0\beta)^2} \quad (3.2)$$

$$= \frac{1}{(1 - k_0\beta^*\rho^*)} + \frac{k_1\beta^*\rho^*}{(1 - k_0\beta^*\rho^*)^2} \quad (3.3)$$

where

V is the molar volume of argon,

$\rho^* = \rho / \rho_c$ is the reduced density of argon,

$\beta^* = \beta\rho_c$, the reduced hard-sphere molar volume of argon, and

ρ_c = the critical density of argon.

Z_{att} obtained by Shah was expressed in the following equation,

$$Z_{att} = -\frac{aV^2 + k_0\beta cV}{V(V + e)(V - k_0\beta)RT} \quad (3.4)$$

where

a and c are parameters that are functions of the temperature, and

e is a constant.

Thus, the attractive pressure term can be written as

$$P_{att} = -\frac{aV + k_0\beta c}{V(V + e)(V - k_0\beta)} \quad (3.5)$$

From Equations (3.1) and (3.5) combined, the generalized quartic EOS has the following form:

$$P = \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V + e)(V - k_0\beta)} \quad (3.6)$$

Therefore, to express a polynomial form in the volume of fourth degree, Equation (3.6) can be rewritten as:

$$V^4 + q_3 V^3 + q_2 V^2 + q_1 V + q_0 = 0 \quad (3.7)$$

where

$$q_0 = -\frac{ck_0^2\beta^2}{P} \quad (3.8)$$

$$q_1 = e\left(k_0^2\beta^2 + \frac{RT}{P}\beta(k_0 - k_1)\right) + \left(\frac{k_0\beta(c - a)}{P}\right) \quad (3.9)$$

$$q_2 = \left(\frac{RT}{P}[\beta(k_0 - k_1) - e] + k_0\beta(k_0\beta - 2e)\right) + \frac{a}{P} \quad (3.10)$$

$$q_3 = \left(-2k_0\beta + e - \frac{RT}{P}\right) \quad (3.11)$$

The parameter β is the hard-sphere volume of the fluid compiled by Bondi (1968). The value of β at the critical temperature is equal to 0.165 times the critical volume of the fluid in the quartic equation of state. To give the best estimation of various thermodynamic properties of a pure compound, Shah determined the parameters a , c , and e by nonlinear regression. Among the four parameters a , β , c , and e given in reduced forms (as shown below), the parameters a , β , and c represent the temperature dependency of the fluid.

$$\beta = \beta_c \left\{ \exp \left[-0.03125 \ln(T_r) - 0.0054 [\ln(T_r)]^2 \right] \right\}^3 \quad (3.12)$$

where

β_c is the hard-sphere volume at the critical temperature, and
 $\beta_c = 0.165 V_c$.

$$a = a_c \alpha(T_r) \quad (3.13)$$

where for $T_r \leq 1$

$$\alpha(T_r) = \left[1 + X_2 (1 - \sqrt{T_r}) + X_3 (1 - \sqrt{T_r})^2 + X_4 (1 - \sqrt{T_r})^3 \right]^2 \quad (3.14)$$

and for $T_r > 1$

$$\alpha(T_r) = \left[1 + X_2 (1 - \sqrt{T_r}) + X_5 (1 - \sqrt{T_r})^2 + X_6 (1 - \sqrt{T_r})^3 \right]^2 \quad (3.15)$$

for the temperature-dependent functional form of c used by nonlinear regressions,

$$c = c_c \xi(T_r) \quad (3.16)$$

$$\xi(T_r) = [1 + X_7(1 - \sqrt{T_r})]^2 \quad (3.17)$$

where

a_c and c_c are the values of a and c at the critical temperature of the fluid, and

X_2 , X_3 , X_4 , X_5 , X_6 , and X_7 are the coefficients determined by nonlinear regression.

For nonpolar fluids the generalized quartic EOS used the acentric factor as the third property of the fluid. The acentric factor used, which comes from the Pitzer's acentric factor (1955), can be obtained by the following equation

$$\omega = -\log_{10} \left(\frac{P_s}{P_c} \right)_{\frac{T}{T_c}=0.7} \quad (3.18)$$

where

P_s is the saturated vapor pressure of the fluid at the reduced temperature of 0.7.

The regressed coefficients X_2 through X_7 , a_c , c_c , and e were made functions of the acentric factor (ω). The regressed coefficients X_2

through X_7 were assumed to be linear functions of ω , and the regressed coefficients a_r , c_r , and e_r were assumed to be quadratic functions of ω . These coefficients are expressed as follows:

$$X_i = X_{i1} + X_{i2}\omega \quad \text{for } i = 2,3,4,5,6, \text{ and } 7. \quad (3.19)$$

$$a_c = \frac{a_r RT_c}{\rho_c} \quad (3.20)$$

$$c_c = \frac{c_r RT_c}{\rho_c} \quad (3.21)$$

$$e = \frac{e_r}{\rho_c} \quad (3.22)$$

$$a_r = a_{r0} (1 + a_{r1}\omega + a_{r2}\omega^2) \quad (3.23)$$

$$c_r = c_{r0} (1 + c_{r1}\omega + c_{r2}\omega^2) \quad (3.24)$$

$$e_r = e_{r0} (1 + e_{r1}\omega + e_{r2}\omega^2) \quad (3.25)$$

$$\beta_r = \beta_c \rho_c \quad (3.26)$$

Equation (3.26) was used to express a dimensionless form of the hard-sphere volume at the critical temperature.

Therefore, for nonpolar fluids Equations (3.12) through (3.26) constitute the generalized quartic equation coefficients in terms of the critical temperature, the critical volume, and the acentric factor. This quartic equation of state contained four parameters. The parameters a , and c were functions of temperature and the acentric factor of the fluid; the parameter β was a function of temperature and was not dependent on the nature of the fluid; and the parameter e was assumed to be a function of the acentric factor of the fluid.

Shah regressed values of the coefficients in Equations (3.19), (3.23), (3.24), and (3.25) from thermodynamic properties data of 16 pure nonpolar fluids. The generalized quartic EOS was then used to predict the thermodynamic properties of other nonpolar fluids, such as benzene and ethylene, not used in the regressions based on only the critical temperature, the critical volume, and the acentric factor.

3.2 An Extension of the Quartic Equation of State to Pure Polar Fluids

To extend the generalized quartic EOS to polar fluids, the fourth property of the fluid, the first moment of the electric charge density of a molecule, was taken into account in this study. Due to the properties of strongly polar fluids, some of their thermodynamic properties cannot be represented very well by two-parameter or three-parameter EOS, which do so well for nonpolar fluids. Without considering the fourth property for polar fluids, such as the dipole, quadrupole, or octupole moment, most traditional cubic EOSs merely introduce the parameter a , the attractive pressure term, as a function of the acentric factor or the compressibility factor in polar systems. However, the resulting equations could not fit the experimental data very well when considering the thermodynamic properties of polar fluids in the supercritical region and saturated liquid density of polar fluids.

Most EOSs do not consider the polarity of the polar fluid, which may be characterized by the dipole, quadrupole, or octupole moment,

which results in additional attractive forces between molecules. Thus, an additional property of the fluid, the dipole moment, is suggested in this investigation since the polarity can be measured by the dipole moment; however, some fluids do not have a dipole moment but have large quadrupole, octupole, or higher electric moments. For instance, the evaluation of thermodynamic properties of carbon dioxide specified only by its critical temperature, critical volume, and acentric factor has been tested successfully using the generalized quartic EOS developed by Shah. However, even though carbon dioxide possesses a quadrupole moment, it is still treated in the same manner as a nonpolar fluid in this work. Therefore, this work concentrates on the dipole moment when considering pure polar fluids.

Since the generalized quartic EOS was developed for nonpolar fluids, a particular interest of this research is directed at extending the quartic EOS to be in agreement with experimental data for polar fluids. To apply the quartic equation of state to polar compounds, the parameters a and c are extended by assuming them to be functions of the acentric factor and the dipole moment while introducing the fourth property of the fluid into the quartic EOS. However, to express the parameters of the quartic equation in dimensionless form, the reduced dipole moment (μ^*) is used, as shown below:

$$\mu^* = \frac{0.3976\mu}{(RT_c V_c)^{0.5}} \quad (3.27)$$

where

μ is the dipole moment of the polar fluid in debye units.

Thus, when investigating the polar fluids, the regressed coefficients X_2 through X_7 were made a linear function of the acentric factor and a quadratic function of the dipole moment. Also, the regressed coefficients a_r and c_r were made quadratic functions of the acentric factor and the reduced dipole moment. Equations (3.19), (3.23), and (3.24) were rewritten in the following forms:

$$X_i = X_{i1} + X_{i2}\omega + X_{i3}\mu^* + X_{i4}\mu^{*2} \quad \text{for } i = 2,3,4,5,6, \text{ and } 7 \quad (3.28)$$

$$a_r = a_{r0} \left(1 + a_{r1}\omega + a_{r2}\omega^2 + a_{r3}\mu^* + a_{r4}\mu^{*2} \right) \quad (3.29)$$

$$c_r = c_{r0} \left(1 + c_{r1}\omega + c_{r2}\omega^2 + c_{r3}\mu^* + c_{r4}\mu^{*2} \right) \quad (3.30)$$

Finally, replacing Equations (3.19), (3.23), and (3.24) with Equations (3.28), (3.29), and (3.30), the generalized quartic equation coefficients for polar fluids are expressed by Equations (3.12) through (3.26). Hence, only requiring four properties of the fluid-the critical temperature, the critical volume, the acentric factor, and the dipole moment-the generalized quartic EOS is extended to predict the behavior of polar fluids. Then, a new set of regressed coefficients applicable to nonpolar and polar fluids is generated using the nonlinear regression algorithm. If the dipole moment of the fluid is zero, then the entire system is simplified as a nonpolar fluid system. To test this nonpolar system using the generalized quartic equation,

only the critical temperature, the critical volume, and the acentric factor are needed.

3.3 The Evaluation of Thermodynamic Properties of the Fluids Using the Quartic Equation of State

Along the vapor-liquid phase envelope, the saturated vapor and liquid densities were determined by using the equilibrium criterion, the equality of the fugacities imposed along the saturation curve. A mathematical form for the equilibrium criterion in the two-phase region can be expressed by

$$f^v = f^l \quad (3.31)$$

where

f^v is the vapor-phase fugacity, and

f^l is the liquid-phase fugacity.

The fugacity of a pure fluid can be calculated using the volumetric equation of state and Equation (3.32):

$$\ln \frac{f(T, P)}{P} = \frac{1}{RT} \int_{V=\infty}^{V=\frac{ZRT}{P}} \left(\frac{RT}{V} - P \right) dV - \ln Z + (Z - 1) \quad (3.32)$$

The generalized quartic equation of state in Equation (3.32) yields

$$\ln \left| \frac{f}{P} \right| = -\ln \left(\frac{V - k_0 \beta}{V} \right) + \frac{k_1 \beta}{(V - k_0 \beta)} - \frac{c}{RTe} \ln \left(\frac{V}{V - k_0 \beta} \right)$$

$$-\frac{(ae - k_0\beta c)}{RT(k_0\beta e + e^2)} \ln\left(\frac{V + e}{V - k_0\beta}\right) - \ln Z + (Z - 1) \quad (3.32)$$

where

f is the fugacity of the fluid.

The vapor-liquid equilibrium pressure of a pure fluid as a function of temperature can be computed using the volumetric equation of state. The calculations are straightforward in principle; however, with the iteration of computations involved, they are best done on a computer to save time. To calculate the vapor pressure of a pure fluid, the Newton-Raphson method was used as an iterative approach to locate the vapor and liquid roots to satisfy Equation (3.31).

The departure function for the enthalpy using the generalized quartic equation of state can be formed by the following equation (Shah, 1992):

$$\begin{aligned} H(T, P) - H^{IG}(T, P) &= \int_V^\infty \left[P - T \left(\frac{\partial P}{\partial V} \right) \right] dV + (PV - RT) \\ &= -\frac{RT^2\beta'(k_0 + k_1)}{(V - k_0\beta)} + \frac{(a + c)Tk_0^2\beta'\beta}{k_0\beta(k_0\beta + e)(V - k_0\beta)} - \frac{k_1k_0\beta'\beta RT^2}{(V - k_0\beta)^2} \\ &\quad + \left\{ \frac{k_0[(c'\beta + c\beta')T - c\beta] - Tk_0\beta'c}{k_0\beta e} \right\} \times \ln\left(\frac{V}{V - k_0\beta}\right) \end{aligned}$$

$$\begin{aligned}
& + \left\{ \frac{(a' T - a)e - k_0 [(c' \beta + c \beta') T - c \beta]}{e(k_0 \beta + e)} - \frac{T k_0 \beta' (ae - c k_0 \beta)}{e(k_0 \beta + e)^2} \right\} \\
& \times \ln \left(\frac{V + e}{V - k_0 \beta} \right) + (PV - RT)
\end{aligned} \tag{3.35}$$

where

a' , β' , and c' are the first derivatives of a , β , and c with respect to the temperature.

To calculate the second virial coefficient, a mathematical form obtained (Shah, 1992) using the quartic EOS was expressed by

$$B_v = (k_0 + k_1) \beta - \frac{a}{RT} \tag{3.36}$$

The thermodynamic properties of pure fluids, the pressure-volume-temperature behavior, the saturation densities, the vapor pressure, the enthalpy departure, and the enthalpy of vaporization, are used to determine the regressed coefficients of the quartic EOS for polar fluids.

3.4 The Regression Technique

In this study the Nelder-Mead simplex algorithm (Nelder, 1965 and Nash, 1987) and an adaptive nonlinear least-squares algorithm (Dennis, 1981) were used to determine the regressed coefficients in

the nonlinear regressions. The former is an efficiently direct search technique for locating the minimum of a function involving a moderate number of parameters and can be applied to problems that are discontinuous. The latter can improve the convergence from poor initial guesses when the iterations approach a local solution. Thus, the former method is used to make the value of the sum-of-squares function move out of a local solution region, and the latter method is used from that point to quickly converge the value to a satisfactory solution.

The experimental data established for polar fluids were fitted by minimizing the following objective function (Shah, 1992) using nonlinear regression algorithms:

$$F = \sum_{i=1}^{N_1} \left[\left(\frac{\Delta P_{s,i}}{P_{s,i}} \right)^2 + \left(\frac{\Delta \rho_{sv,i}}{\rho_{sv,i}} \right)^2 + \left(\frac{\Delta \rho_{sl,i}}{\rho_{sl,i}} \right)^2 \right] + \sum_{j=1}^{N_2} \left(\frac{\Delta \rho_{g,j}}{\rho_{g,j}} \right)^2 + \sum_{k=1}^{N_3} \left(\frac{\Delta H_{r,k}}{H_{r,k}} \right)^2 + \sum_{l=1}^{N_4} \left(\frac{\Delta H_{vap,l}}{H_{vap,l}} \right)^2 + \sum_{m=1}^{N_5} \left(\frac{\Delta B_{v,m}}{B_{v,m}} \right)^2 \quad (3.37)$$

where

N_1 is the number of saturation data points in the two-phase region,

N_2 is the number of gas density data points in the single-phase region,

N_3 is the number of residual enthalpy data points,

N_4 is the number of enthalpy of vaporization data points in the two-phase region,

N_5 is the number of second virial coefficient data points,

P_s is the saturated vapor pressure,

ρ_{sv} is the saturated vapor density,

ρ_{sl} is the saturated liquid density,

H_r is the residual enthalpy,

H_{vap} is the enthalpy of vaporization,

B_v is the second virial coefficient,

$\Delta P_s = (P_s^{calc} - P_s^{exp})$ is the error in the saturated vapor pressure,

$\Delta \rho_{sv} = (\rho_{sv}^{calc} - \rho_{sv}^{exp})$ is the error in the saturated vapor density,

$\Delta \rho_{sl} = (\rho_{sl}^{calc} - \rho_{sl}^{exp})$ is the error in the saturated liquid density,

$\Delta \rho_g = (\rho_g^{calc} - \rho_g^{exp})$ is the error in the gas density,

$\Delta H_r = (H_r^{calc} - H_r^{exp})$ is the error in the residual enthalpy,

$\Delta H_{vap} = (H_{vap}^{calc} - H_{vap}^{exp})$ is the error in the enthalpy of

vaporization, and

$\Delta B_v = (B_v^{calc} - B_v^{exp})$ is the error in the second virial coefficient.

The criterion for determination of the regressed coefficients with which we are concerned in this study is the deviation between the calculated and experimental data for pure polar systems. The objective function, Equation (3.37), contains the evaluations of various thermodynamic properties of a pure polar compound, which are described in 3.3. Thus, defined multiproperty regressions were used to locate the new regressed coefficients corresponding to the items of the reduced dipole moment. The previously reported

regressed coefficients (Shah, 1992) for nonpolar fluids were kept constant during regressions for 30 pure polar compounds. Near the critical region, approximately $0.97 - 1.0T_r$, the experimental data for the vapor pressure and saturation densities were not adopted during regressions. A brief procedure for determining the regressed coefficients using computer programs (Shah, 1992) that are modified for polar fluids is summarized in Appendix A.

To this end, the generalized quartic EOS is applicable to polar fluids by modifying the temperature dependence of the parameters, a and c , as functions of the acentric factor and the dipole moment of the fluid. A reduced form representing the dipole moment of the fluid is reported for the development of a quartic EOS for polar fluids. Thermodynamic properties calculated using the quartic EOS in this study are described. Application of the multiproperty regression analysis for obtaining the optimum regressed coefficients is also reported. Therefore, for polar fluids, an investigation of the quartic EOS to estimate the dependence of the parameters a , c , and e on the temperature, the acentric factor, and the dipole moment of the fluid is made using the multiproperty nonlinear regressions.

CHAPTER 4

RESULTS AND DISCUSSION

The new generalized quartic EOS has been applied to calculate physical and thermodynamic properties of 30 polar compounds, such as refrigerants, esters, ethers, ketones, alcohols, etc. These physical and thermodynamic properties were taken from experimental literature values for 30 polar compounds, which constitute the database. The investigation described in this chapter is concerned with the result of obtaining a new set of regressed coefficients, which also include the original regressed coefficients for nonpolar fluids, for polar fluids using the generalized quartic EOS. The performance of the generalized quartic EOS in evaluating various physical and thermodynamic properties of polar fluids is demonstrated. The Peng-Robinson equation has been widely used for calculating various thermodynamic properties of pure compounds and their mixtures in the chemical industry, due to its relative accuracy and simplicity, compared to more complex equations. Thus, a comparison of the capability of the generalized quartic EOS to predict various physical and thermodynamic properties with that of the Peng-Robinson is also taken into account in this chapter.

The parameters in the generalized quartic EOS are expressed by the nondimensional forms. Thus, the reduced dipole moment,

expressed in terms of the critical temperature, the critical volume, and the dipole moment, is used to represent the dipole moment of the fluid. To determine this new set of regressed coefficients, the parameters, a and c , of the generalized quartic EOS have been made functions of the acentric factor and the dipole moment of the fluids. The validity of this assumption is proven by plotting the reduced dipole moment against the acentric factor, as shown in Figure 4.1. The correlation between the acentric factor and the reduced dipole moment of 30 polar fluids illustrated in Figure 4.1 shows that the acentric factor is only weakly correlated with the reduced dipole moment. Therefore, four properties of the fluid, the critical temperature, the critical volume, the acentric factor, and the dipole moment, characterize this generalized quartic EOS. The data ranges and data sources of 30 pure polar compounds are given in Table 4.1. In addition, Appendix B presents a detailed description of data ranges of the various thermodynamic properties used in the regressions for each compound. Table 4.2 shows the critical properties, the acentric factor, and the dipole moment of pure polar compounds, which are used during the regressions. The sources of pure polar compound properties are adopted from Daubert and Danner (1989).

Table 4.3 reports the new set of regressed coefficients obtained using multiproperty regressions for 30 pure polar compounds. This new set of regressed coefficients is applicable to nonpolar and polar fluids. The major difference between nonpolar and polar fluids in

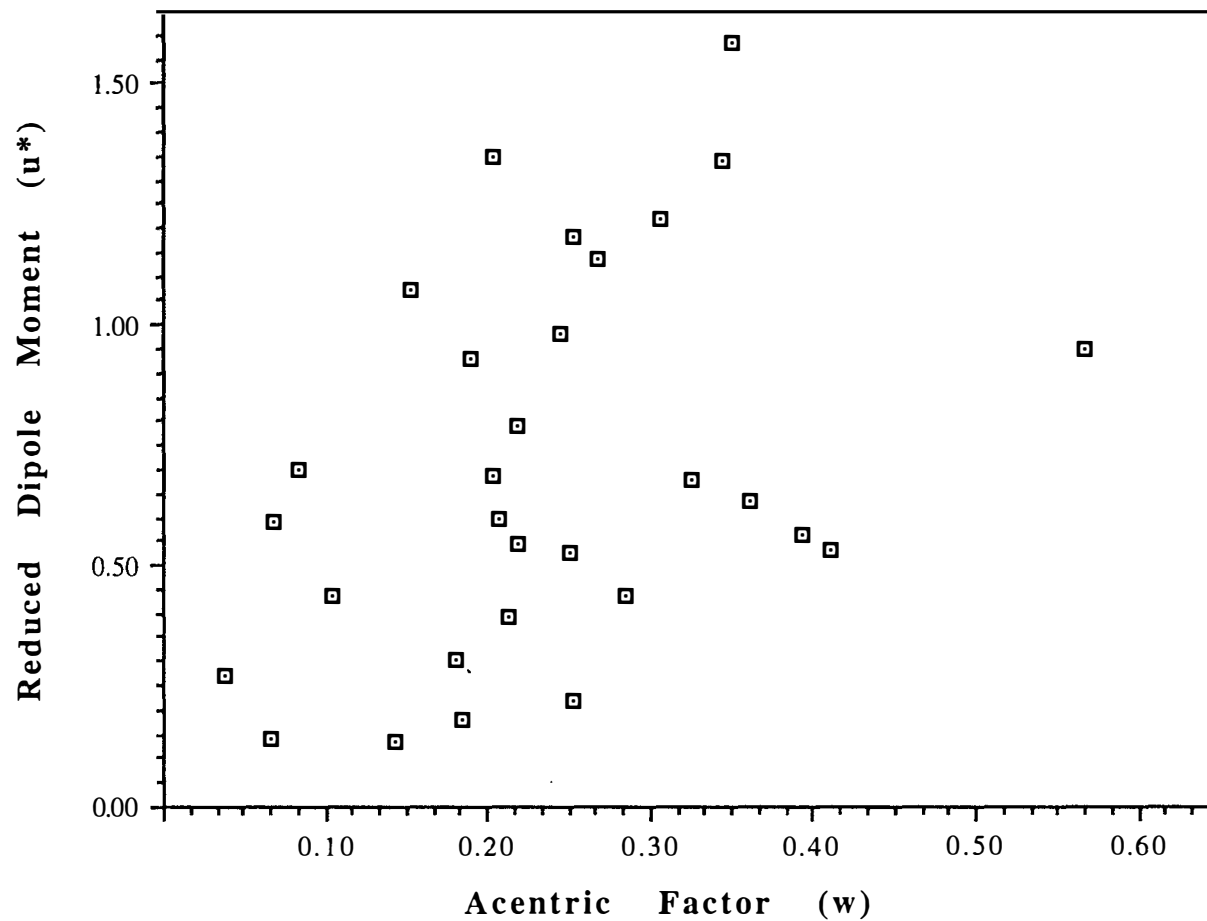


Figure 4.1: Correlation between the reduced dipole moment and the acentric factor for 30 polar fluids

Table 4.1: 30 pure compound data ranges used in the regressions and their data sources (* Appendix E, ** Saturation pressure only)

Compound	Temperature Range (K)	Pressure Range (MPa)	Data Sources*
Acetone	320-1000	0-100	[1], [2]
Carbon Monoxide	68-1000	0-100	[3]
Carbonyl Sulfide	150-680	**	[1]
Methyl Acetate	250-505	**	[1]
Ethyl Acetate	250-650	**	[1]
n-Propyl Acetate	260-620	**	[1]
n-Butyl Acetate	300-750	**	[1]
Freon-11 (CCl_3F)	220-1000	0-50	[1], [2], [4]
Freon-13 (CClF_3)	150-1000	0-50	[2], [4]
Freon-21 (CHFCl_2)	250-1000	0-90	[2], [4]
Freon-22 (CHClF_2)	180-800	0-100	[2], [4], [5], [6]
Freon-23 (CHF_3)	145-600	0-100	[1], [2], [4]
Freon-114 ($\text{C}_2\text{Cl}_2\text{F}_4$)	250-600	0-100	[2], [4]
Methyl Chloride	206-623	0-35	[1], [7], [8]
Methyl Fluoride	167.7-950	**	[1]
Ethyl Chloride	200-450	**	[1]
Chlorform	250-514	**	[1]
Chlorobenzene	353-900	0-100	[1], [2]
Dimethyl Ether	180-396	**	[1]
Diethyl Ether	255-600	0-100	[1], [2]
Methyl Ethyl Ether	320-435	**	[1]
Hydrogen Bromide	200-360	**	[1]
Hydrogen Iodide	230-420	**	[1]
Water	273.16-1273.16	0-100	[1], [6], [9]
Hydrogen Sulfide	200-493	0-170	[1], [2], [10]
Methanol	300-800	0-70	[1], [11]
Ammonia	200-800	0-100	[1], [12]
Nitrous Oxide	190-520	0-32	[1], [13], [14]
Sulfur Dioxide	205-900	0-100	[1], [2], [15]
Acrylonitrile	810-970	**	[1]

Table 4.2: Pure polar compound physical properties of the fluids
used in the regressions [Daubert and Danner (1989)]

Compound	Critical Temperature (K)	Critical Volume (dm ³ /mol)	Acentric Factor	Dipole Moment (debye)
Acetone	508.2	0.209	0.3064	2.880
Carbon Monoxide	132.92	0.0931	0.0663	0.112
Carbonyl Sulfide	378.8	0.1351	0.1041	0.712
Methyl Acetate	506.8	0.228	0.3253	1.679
Ethyl Acetate	523.25	0.286	0.3611	1.780
n-Propyl Acetate	549.4	0.345	0.3935	1.790
n-Butyl Acetate	579.15	0.389	0.4101	1.840
Freon-11 (CCl ₃ F)	471.2	0.248	0.1837	0.450
Freon-13 (CClF ₃)	301.96	0.18028	0.18	0.510
Freon-21 (CHFCl ₂)	451.58	0.196	0.2069	1.290
Freon-22 (CHClF ₂)	369.3	0.166	0.2192	1.420
Freon-23 (CHF ₃)	298.89	0.1333	0.2672	1.649
Freon-114 (C ₂ Cl ₂ F ₄)	418.85	0.29368	0.252	0.560
Methyl Chloride	416.25	0.139	0.1529	1.870

Table 4.2 (cont'd)

Compound	Critical Temperature (K)	Critical Volume (dm ³ /mol)	Acentric Factor	Dipole Moment (debye)
Methyl Fluoride	317.7	0.113	0.2037	1.851
Ethyl Chloride	460.35	0.200	0.1905	2.050
Chloroform	536.4	0.239	0.2129	1.010
Chlorobenzene	632.35	0.308	0.2505	1.690
Dimethyl Ether	400.1	0.170	0.2036	1.300
Diethyl Ether	466.7	0.280	0.2846	1.150
Methyl Ethyl Ether	437.8	0.221	0.2189	1.230
Hydrogen Bromide	363.15	0.10026	0.0693	0.820
Hydrogen Iodide	423.35	0.12194	0.0381	0.440
Water	647.13	0.05595	0.3449	1.850
Hydrogen Sulfide	373.53	0.09849	0.0827	0.970
Methanol	512.58	0.11905	0.5656	1.700
Ammonia	405.65	0.07247	0.2520	1.470
Nitrous Oxide	309.57	0.09737	0.1418	0.167
Sulfur Dioxide	430.75	0.1220	0.2451	1.630
Acrylonitrile	535	0.212	0.3498	3.870

Table 4.3: Quartic equation of state coefficients obtained using nonlinear regressions for 30 pure polar compound data

Regressed Coefficients		Regressed Coefficients	
a_{r0}	1.84713	X_{21}	0.14988
a_{r1}	-0.05218	X_{22}	0.97848
a_{r2}	1.06446	X_{31}	-0.32379
β_r	0.16500	X_{32}	1.84591
c_{r0}	1.78336	X_{41}	0.14833
c_{r1}	-1.29690	X_{42}	-3.46693
c_{r2}	2.78945	X_{51}	0.11048
e_{r0}	0.63189	X_{52}	0.57743
e_{r1}	-0.81660	X_{61}	0.02581
e_{r2}	3.25246	X_{62}	-0.02700
k_0	1.28650	X_{71}	-0.77357
k_1	2.82250	X_{72}	-1.45342
a_{r3}^*	-0.02730	X_{43}^*	-0.39170
a_{r4}^*	0.02048	X_{44}^*	-0.01597
c_{r3}^*	0.07000	X_{53}^*	0.41218
c_{r4}^*	0.01188	X_{54}^*	-0.10676
X_{23}^*	-0.01390	X_{63}^*	0.38327
X_{24}^*	0.02928	X_{64}^*	-0.09008
X_{33}^*	0.39338	X_{73}^*	-0.04725
X_{34}^*	-0.25483	X_{74}^*	-0.09669

* These coefficients corresponding to the items of the reduced dipole moment were varied during regressions. When the reduced dipole moment is equal to zero, these coefficients are not used.

this study lies in the dipole moment. For nonpolar fluids, the terms in Equations (3.28), (3.29), and (3.30) representing the dipole moment are zero. Thus, the new set of regressed coefficients reduce to the previous coefficients reported by Shah (1992) for nonpolar fluids.

As far as the predictions of the two phase envelope and various physical and thermodynamic properties are concerned, the generalized quartic equation of state has exhibited its accuracy and superior capability in calculating these properties for polar fluids. As for polar fluids, most cubic EOSs have been developed to fit the experimental data of vapor pressure well. When these EOSs are used to predict some physical and thermodynamic properties of pure polar fluids in other regions, such as the region above the critical temperature, large deviations appear. Thus, in general, the applicability and flexibility of most cubic EOSs are limited to certain regions when dealing with pure polar compounds.

In order to overcome this disadvantage, the generalized quartic EOS has been developed to be applicable to polar fluids in other regions when evaluating various properties, such as pressure-volume-temperature relations, vapor pressure, saturated vapor density, saturated liquid density, enthalpy departure, enthalpy of vaporization, and the second virial coefficient. Figures 4.2, 4.3, 4.4, and 4.5 plot pressure against density for carbon monoxide, Freon-23 (CHF_3), methyl chloride and Freon-22 (CHClF_2) in the supercritical

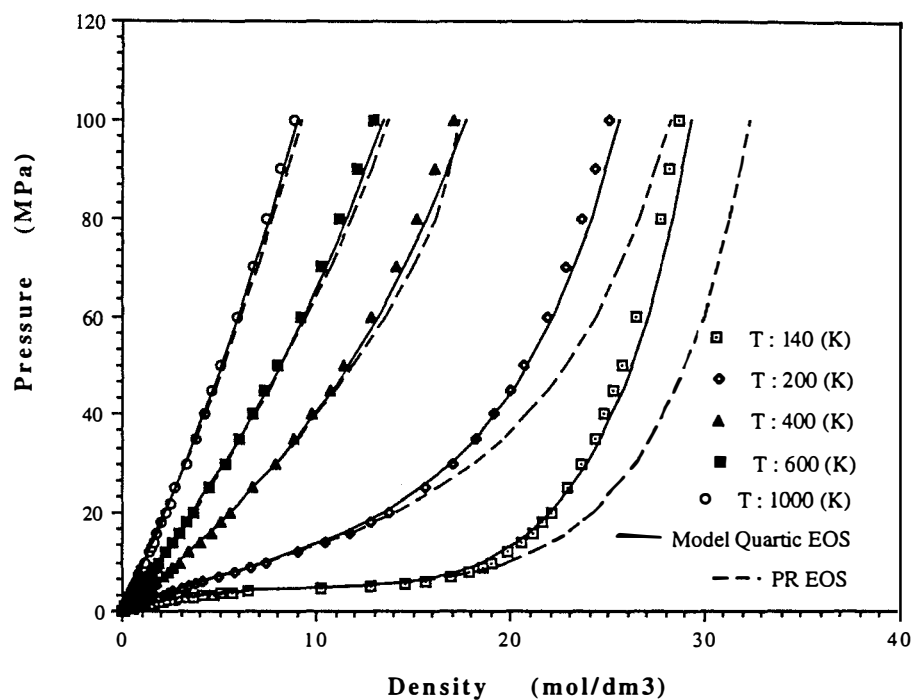


Figure 4.2: Pressure-density calculation for Carbon Monoxide

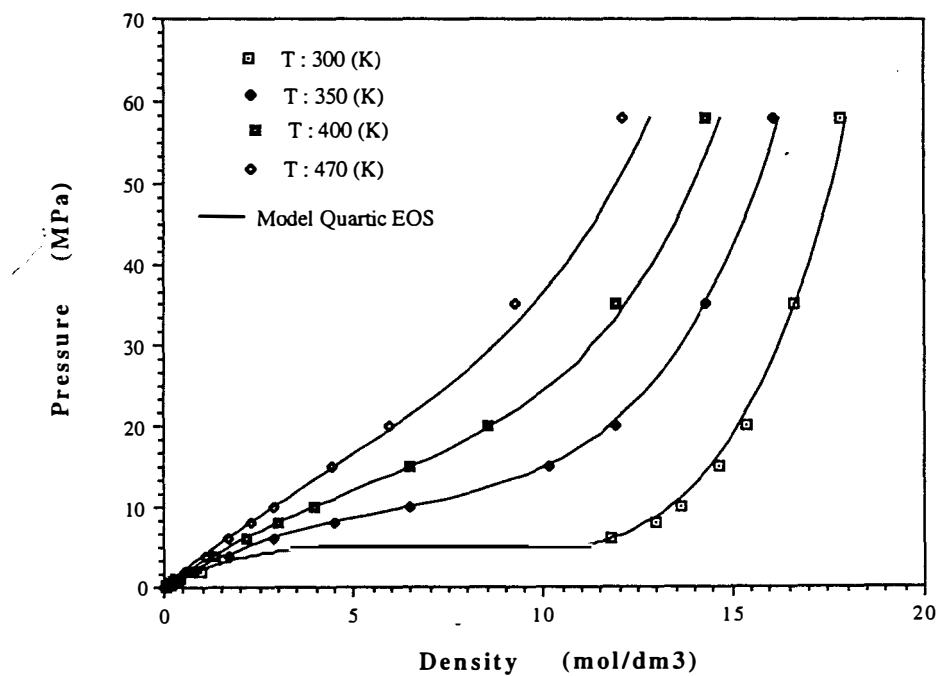


Figure 4.3: Pressure-density calculation for Freon-23 (CHF3)

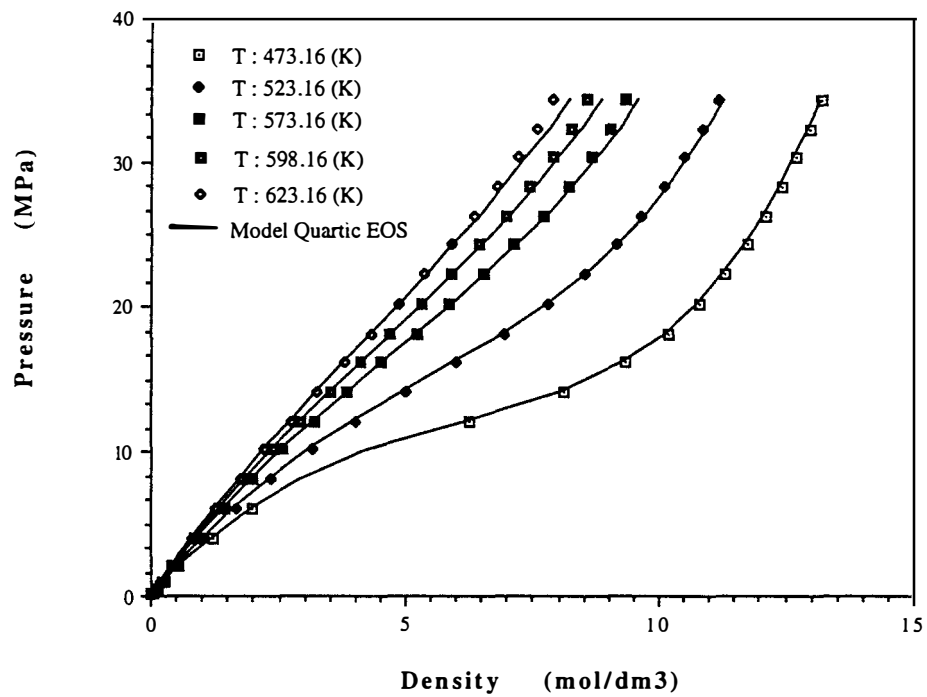


Figure 4.4: Pressure-density calculation for Methyl Chloride

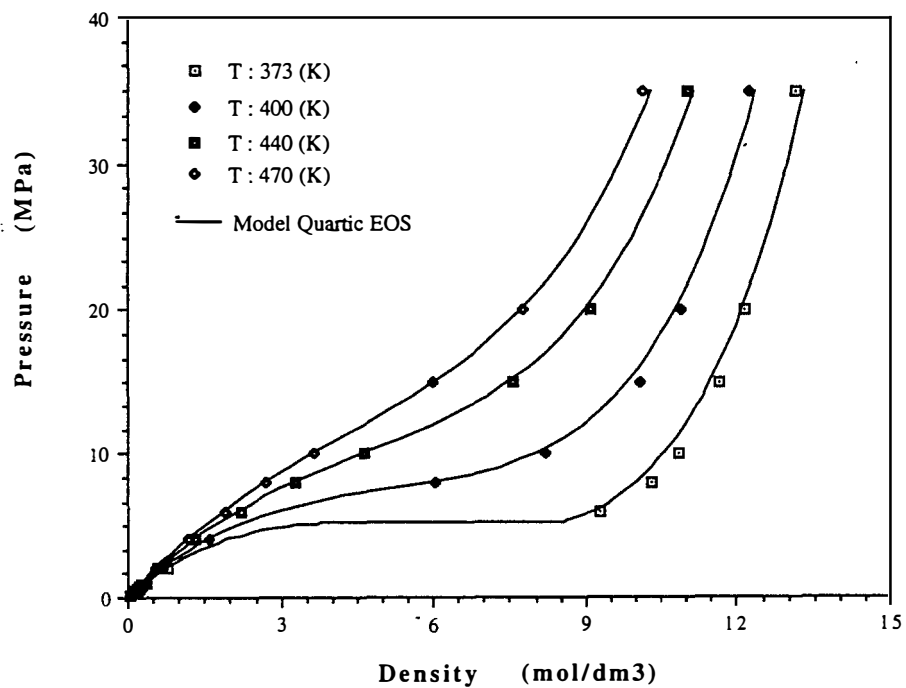


Figure 4.5: Pressure-density calculation for Freon-22(CHClF₂)

region. They show the generalized quartic EOS predicts accurately over a wide range of pressures and densities for polar compounds. A log-log plot of pressure-density calculations for water is shown in Figure 4.6. It presents the capability of the generalized quartic EOS to fit the density of water in the low-pressure range.

The saturated vapor-liquid-equilibrium calculations for Freon-22 (CHClF_2), methyl chloride, ammonia, water, and methanol are presented in Figures 4.7, 4.8, 4.9, 4.10, and 4.11, respectively. The predictions of saturated liquid densities of polar fluids can be seen in those figures. However, these results show that the accuracy achieved is not very reliable near the critical point of the fluid. The reason is that pure polar compound data close to the critical point are not used in searching for a new set of regressed coefficients during the regressions. It was a deliberate decision of this work to sacrifice some accuracy in the critical regions (where no analytical equations can model the critical regions accurately anyway (Sengers and Levelt Sengers, 1986)) in exchanged for improved accuracy over a wide range of temperature-volume states. Figures 4.12, 4.13, 4.14, and 4.15 show the enthalpy departure calculations for chlorobenzene, Freon-11 (CCl_3F), sulfur dioxide, and Freon-11 (CCl_3F). Over a wide range of pressures and temperatures, the generalized quartic EOS shows its superior capability in the enthalpy departure calculations.

The calculations of the second virial coefficient for esters and chlorobenzene can be seen in Figures 4.16 and 4.17, respectively.

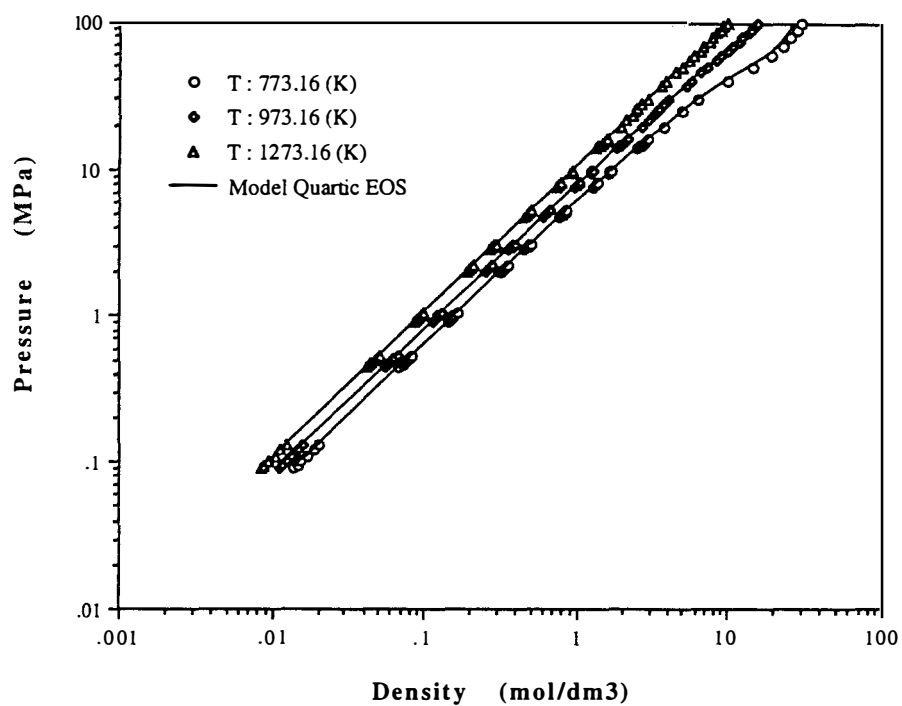


Figure 4.6: Pressure-density calculation for Water

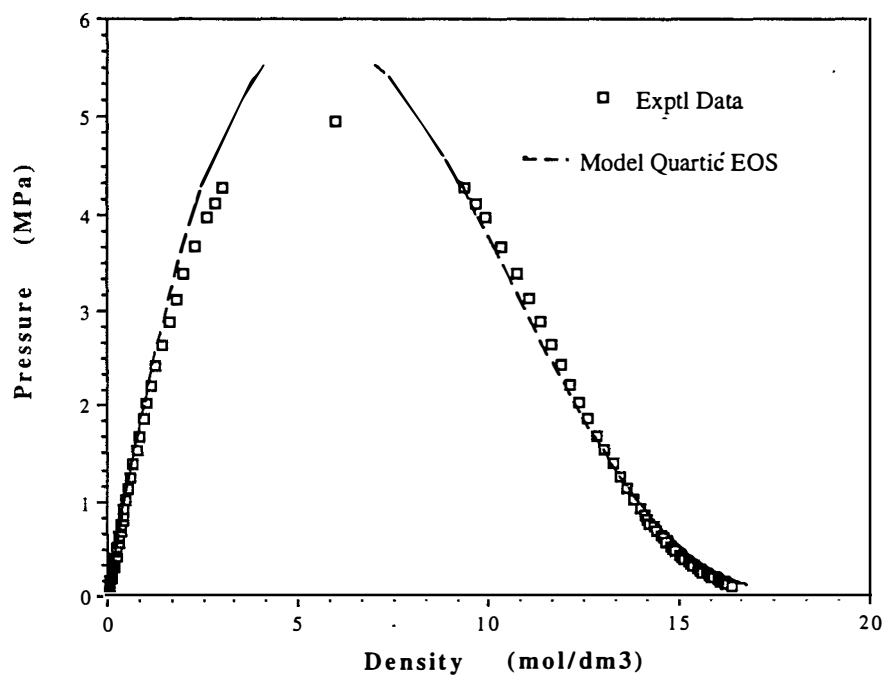


Figure 4.7: Saturated VLE calculation for Freon-22(CHClF2)

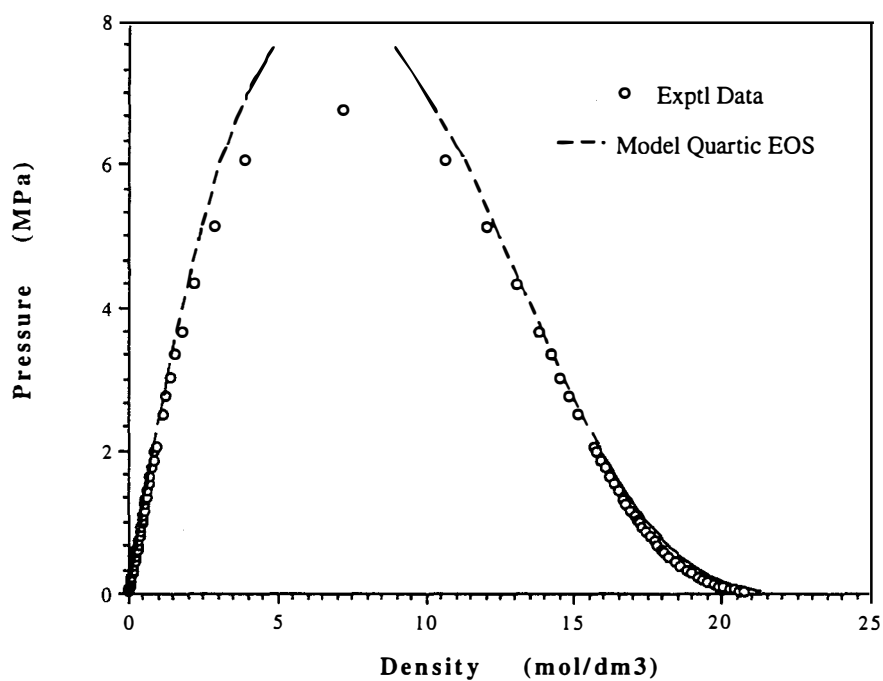


Figure 4.8: Saturated VLE calculation for Methyl Chloride

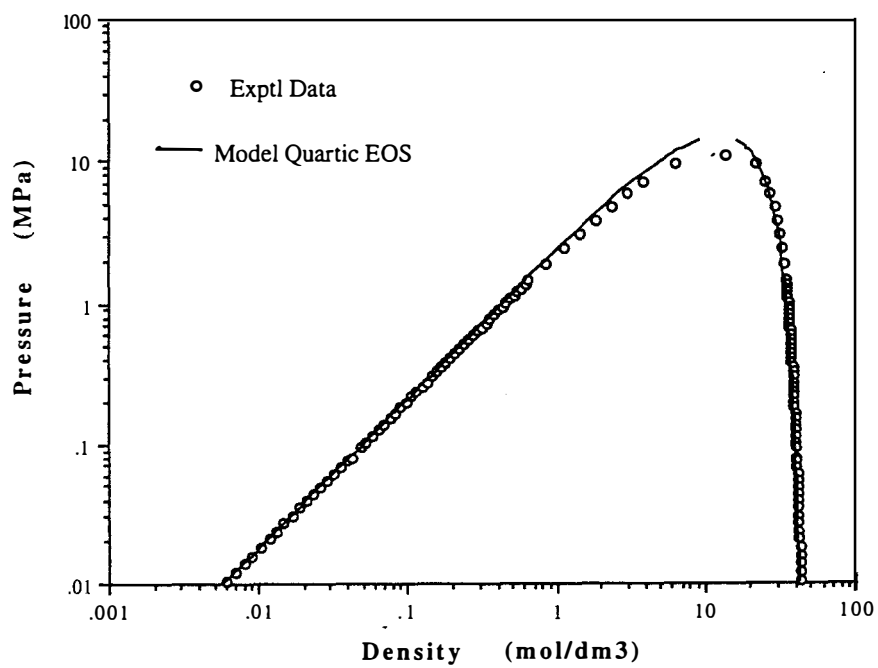


Figure 4.9: Saturated VLE calculation for Ammonia

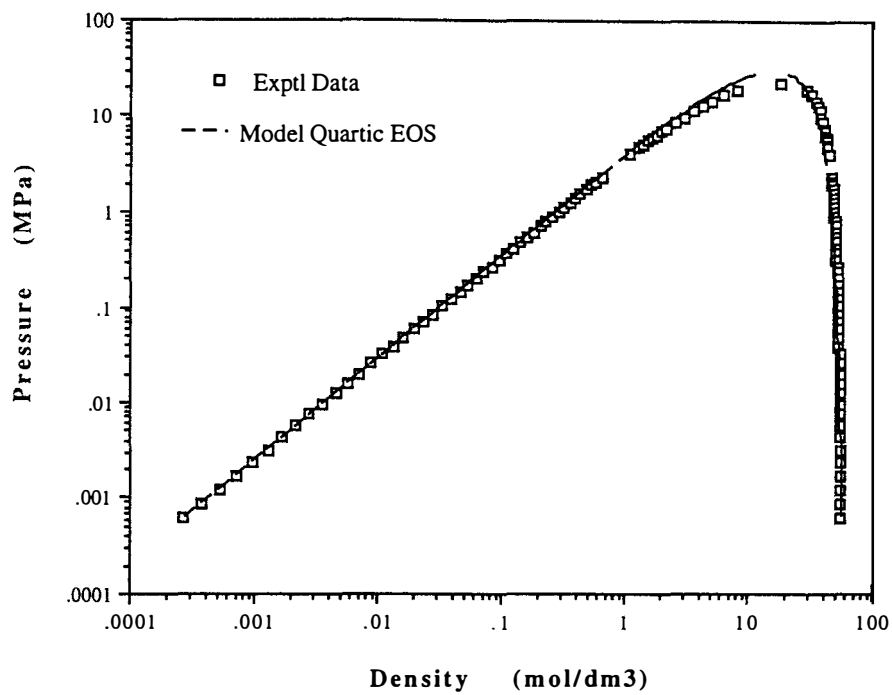


Figure 4.10: Saturated VLE calculation for Water

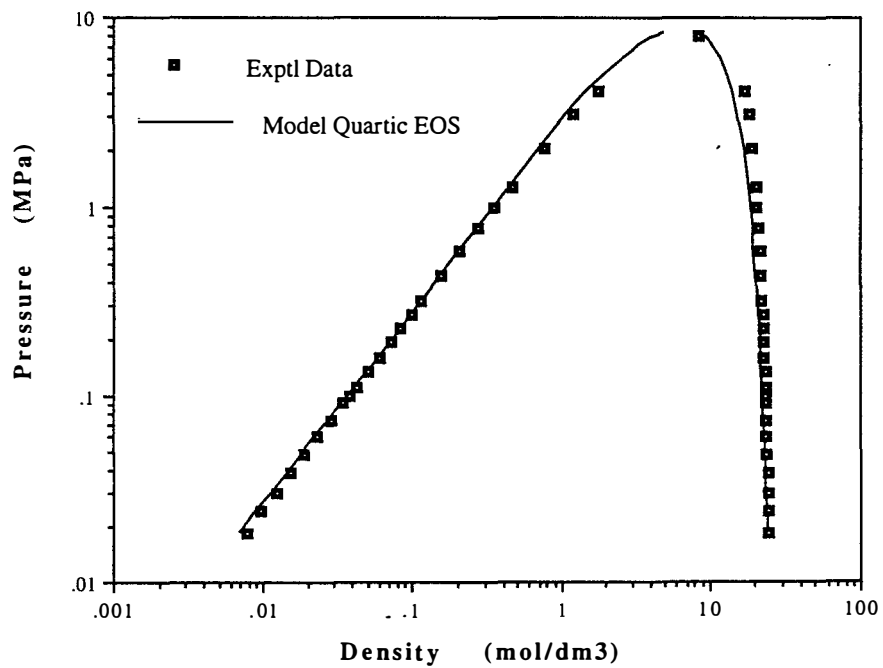


Figure 4.11: Saturated VLE calculation for Methanol

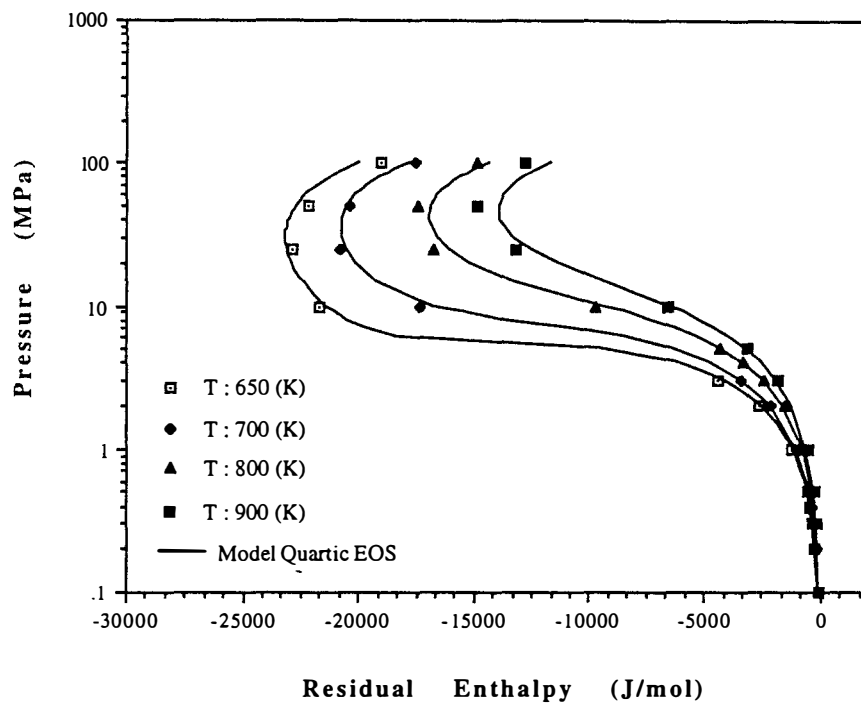


Figure 4.12: Residual enthalpy calculation for Chlorobenzene

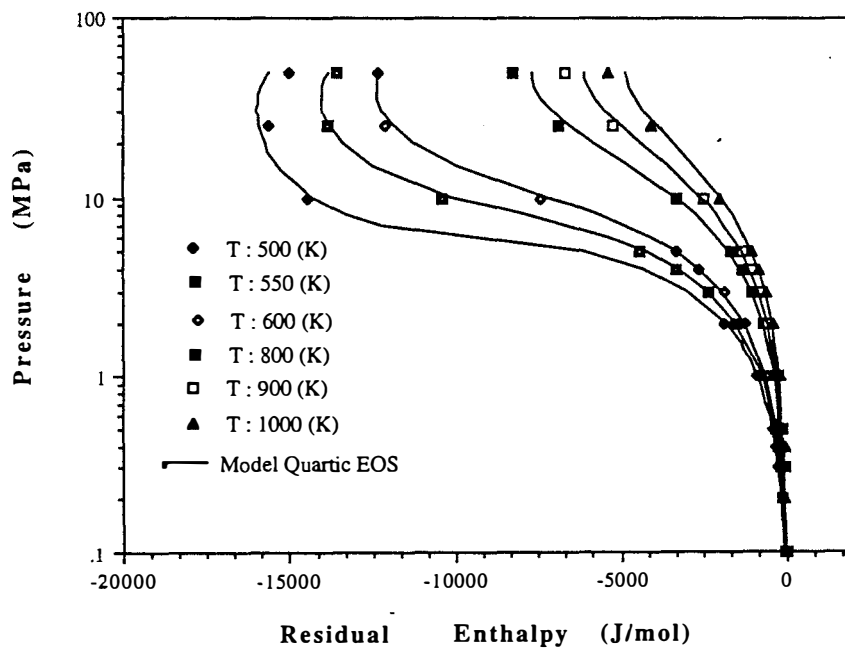


Figure 4.13: Residual enthalpy calculation for Freon-11(CCl_3F)

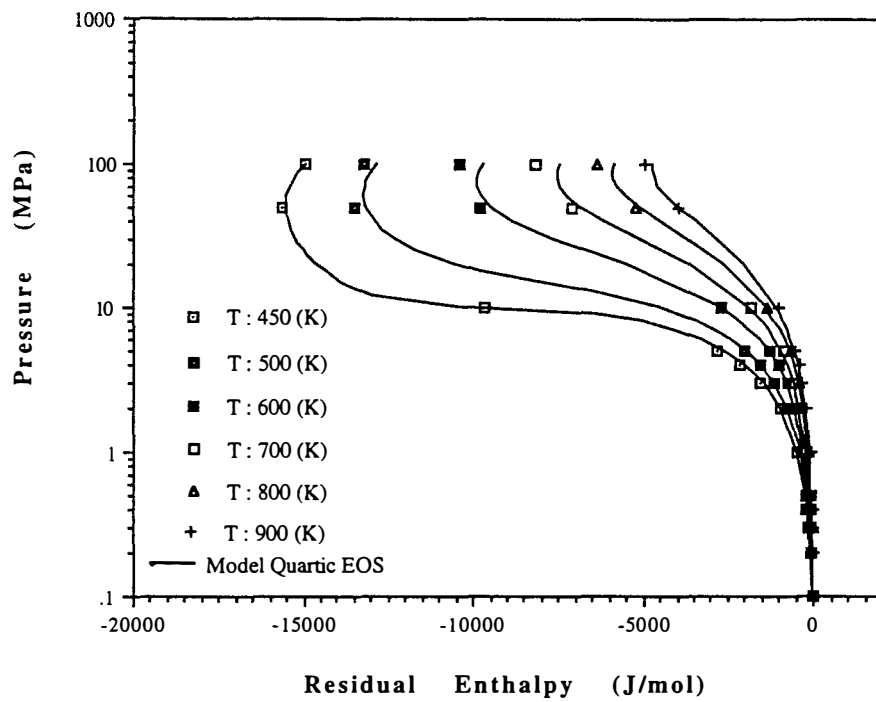


Figure 4.14: Residual enthalpy calculation for Sulfur Dioxide

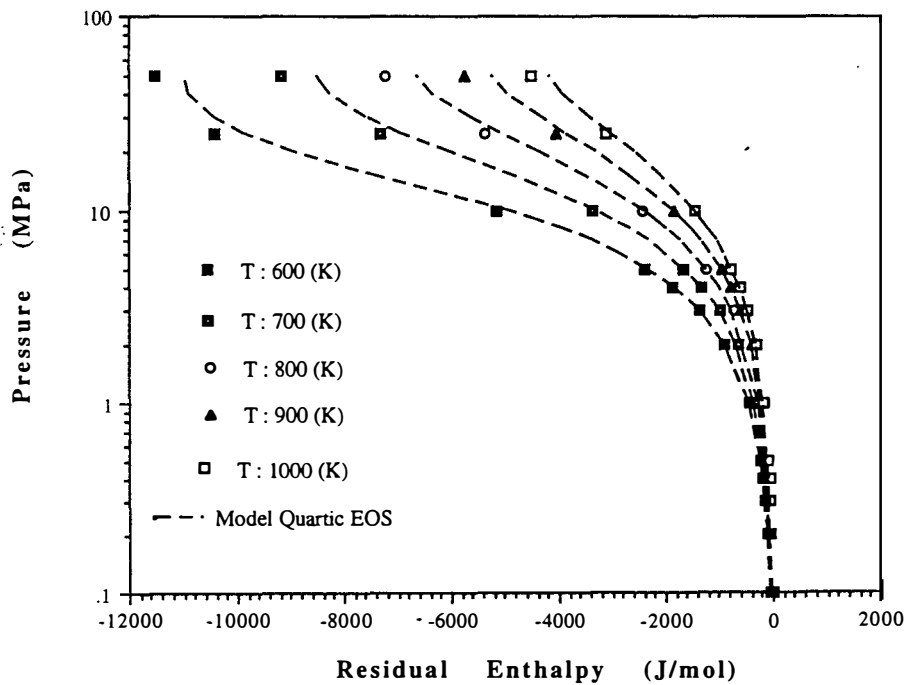


Figure 4.15: Residual enthalpy calculation for Freon-21(CHFC12)

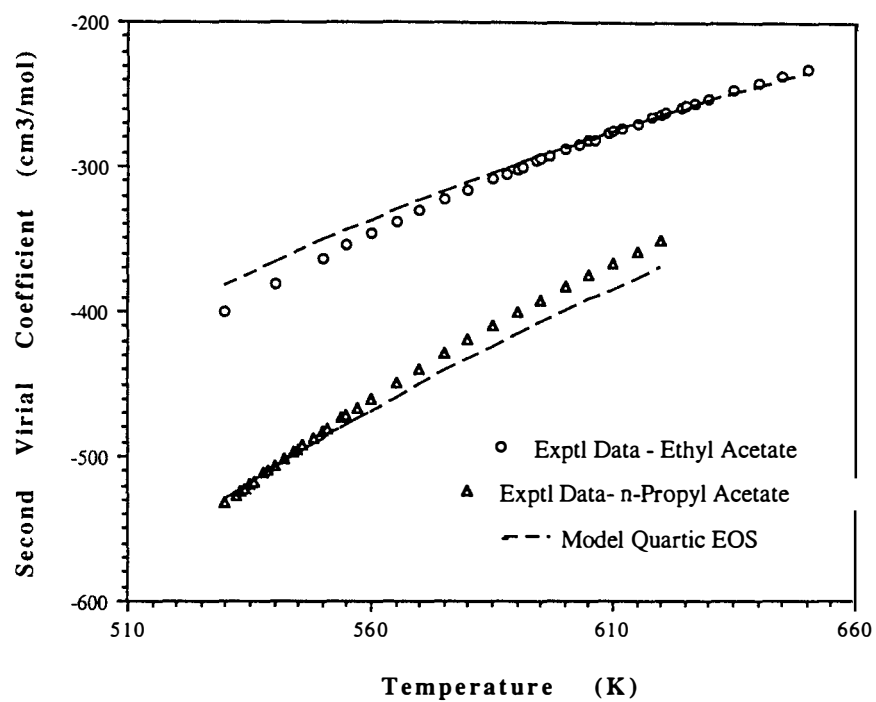


Figure 4.16: Second virial coefficient calculation for Esters

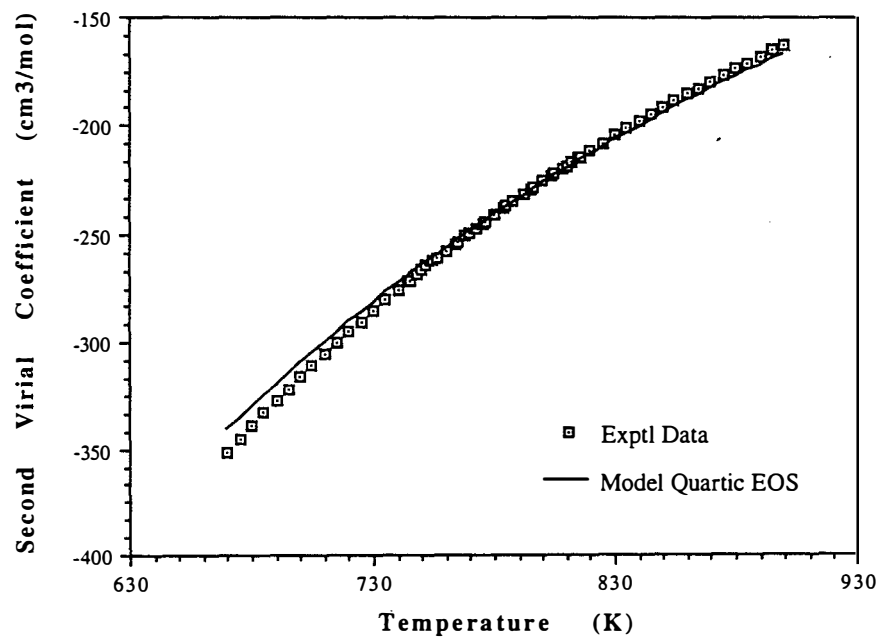


Figure 4.17: Second virial coefficient calculation for Chlorobenzene

The range for the second virial coefficient calculation is still restricted to the supercritical region. Figures 4.18 and 4.19 show the vapor pressure calculations for chloroform and ethers. The calculations of enthalpy of vaporization for Freon-11 (CCl_3F) and butyl acetate are reported in Figures 4.20 and 4.21, respectively.

A comparison of the accuracy and capability of the generalized quartic EOS with those of the widely used Peng-Robinson EOS was made. However, the PR EOS was not refitted using 30 pure polar fluid database and their ranges; the comparison was, therefore, not entirely fair. A comparison of pressure-density calculations for carbon monoxide is presented in Figure 4.2. When the temperature is close to $3T_r$, the two EOSs almost perform equally so that the calculated values are in good agreement with the experimental data. Figure 4.22 shows the calculation of pressure versus density for ammonia at the supercritical region by these two equations of state. The AAD calculation for ammonia was 0.76% for the generalized quartic equation and 1.56% for the Peng-Robinson equation. The Peng-Robinson EOS predicts larger deviations when the temperature approaches the critical temperature from above. Two-phase envelope calculations for water and ammonia using two equations of state are presented in Figures 4.23 and 4.24, respectively. The saturated liquid density calculations, the Peng-Robinson EOS predictions have much larger errors. The AAD calculations of the saturated liquid density for water and ammonia were 3.5% and 0.74% for the generalized quartic equation and 17.59% and 11.86%

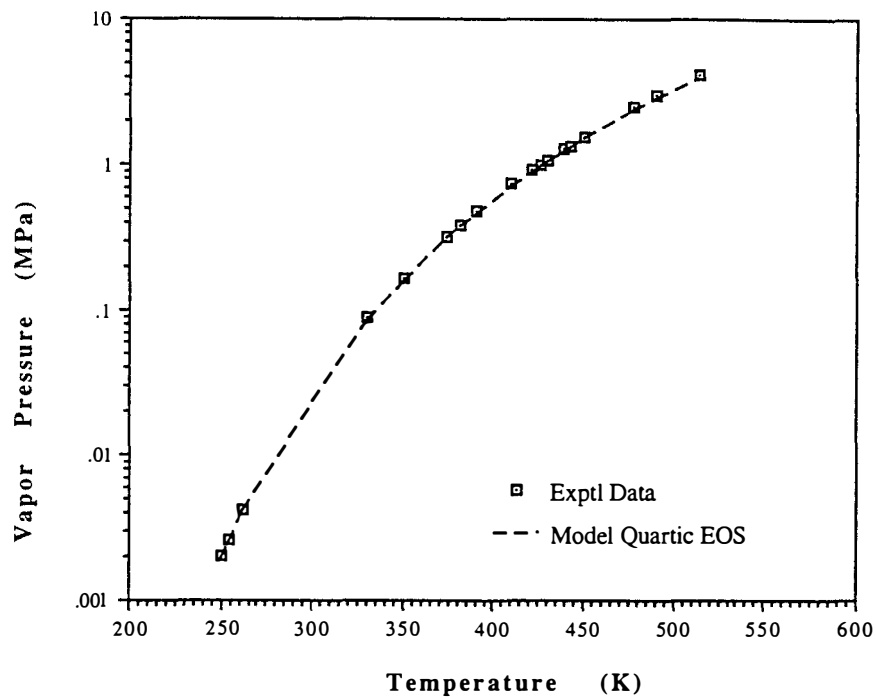


Figure 4.18: Vapor pressure calculation for Chloroform

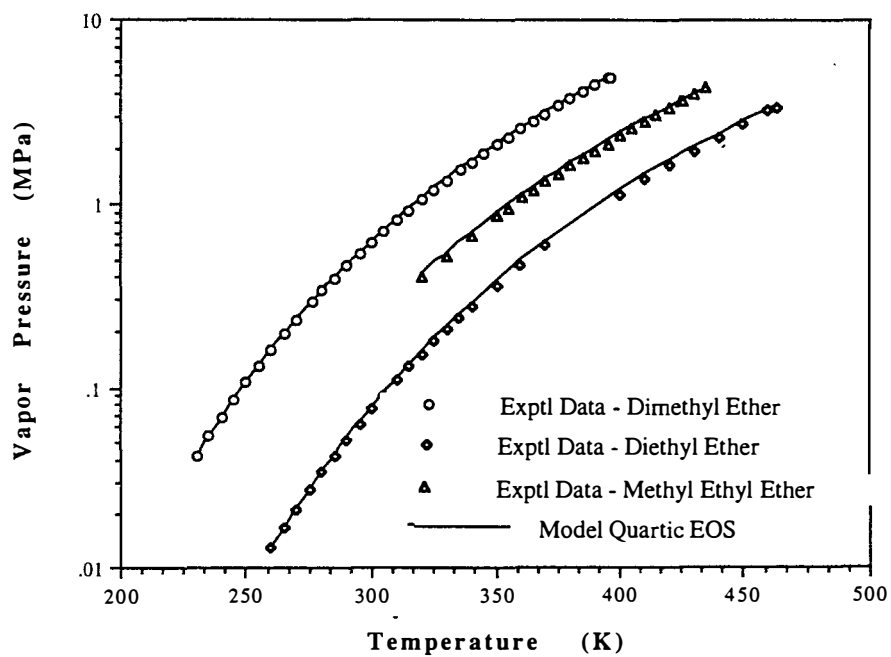


Figure 4.19: Vapor pressure calculation for Ethers

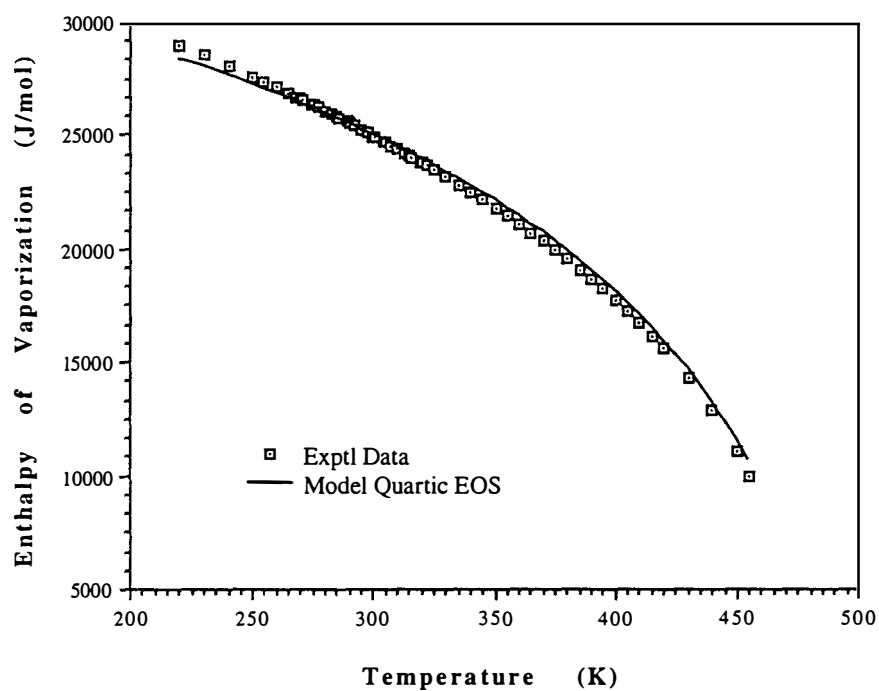


Figure 4.20: Enthalpy of vaporization calculation for Freon-11(CCl_3F)

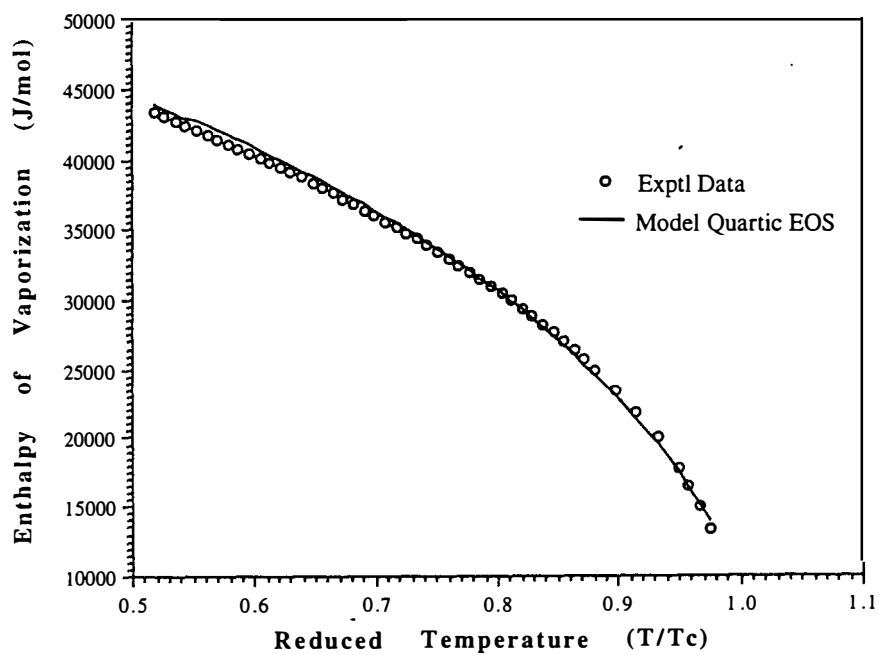


Figure 4.21: Enthalpy of vaporization calculation for Butyl Acetate

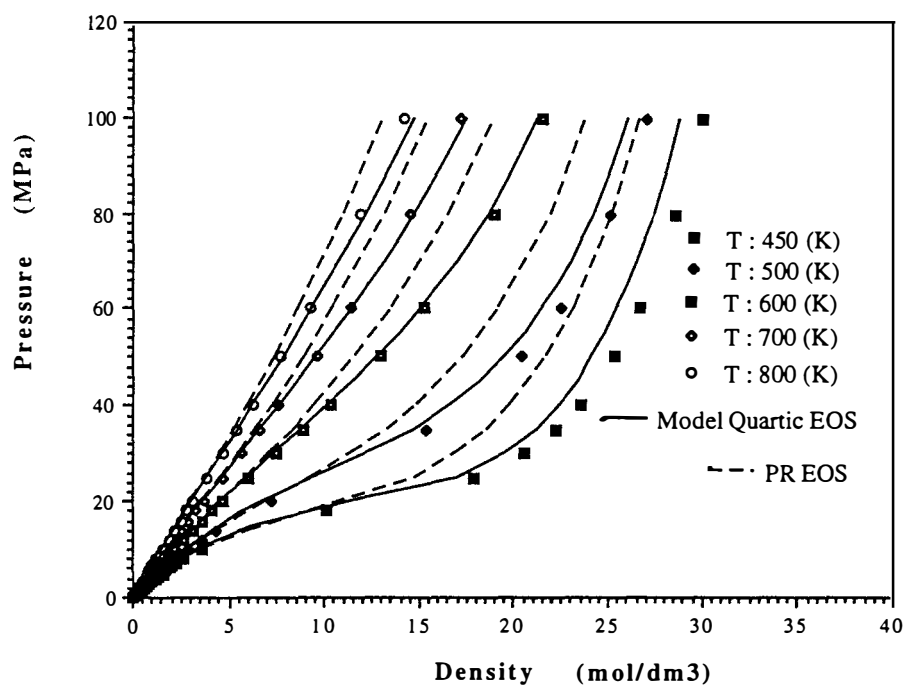


Figure 4.22: Comparison of pressure-density calculation for Ammonia using different equations of state

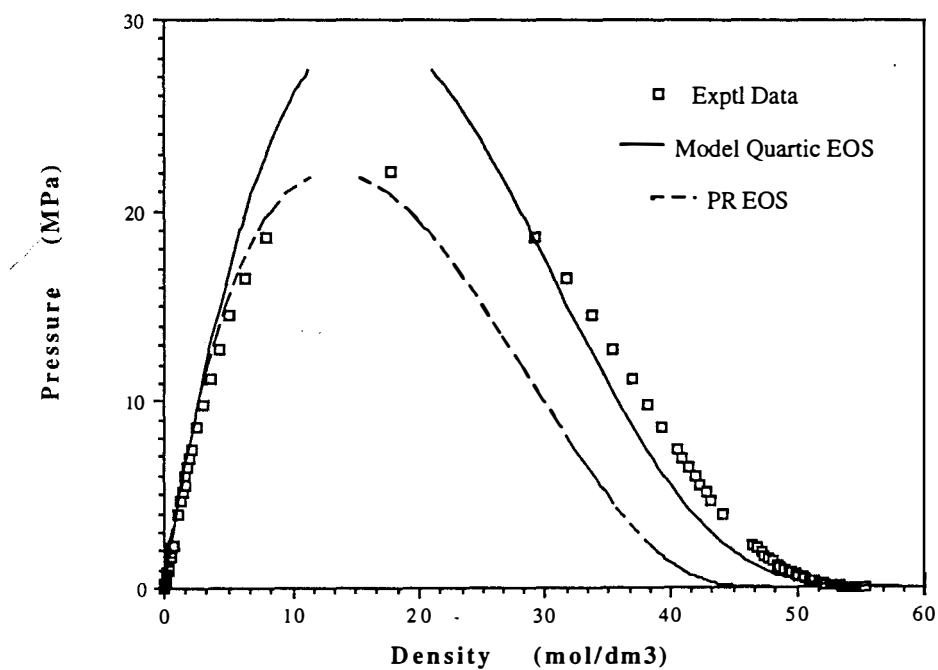


Figure 4.23: Comparison of saturated VLE calculation for Water using different equations of state

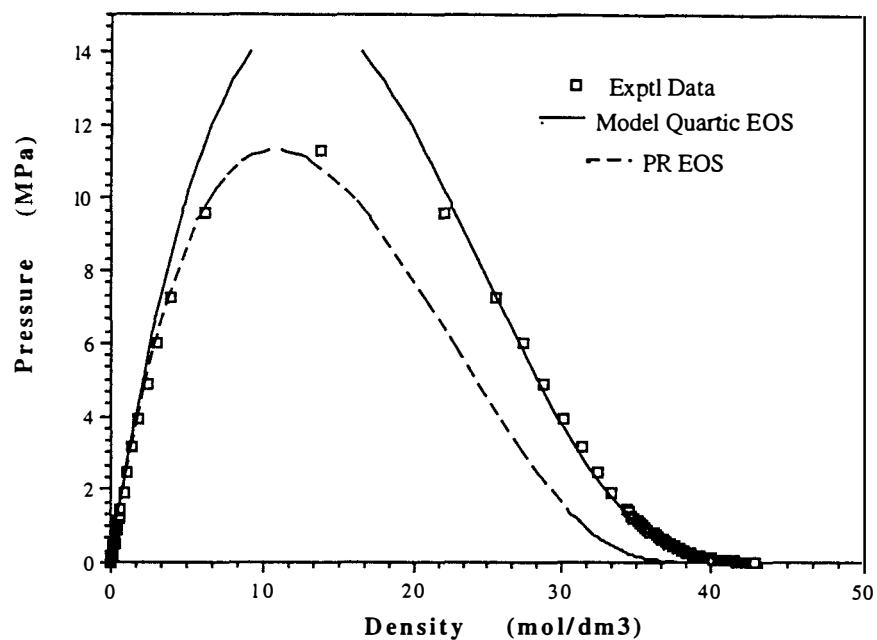


Figure 4.24: Comparison of saturated VLE calculation for Ammonia using different equations of state

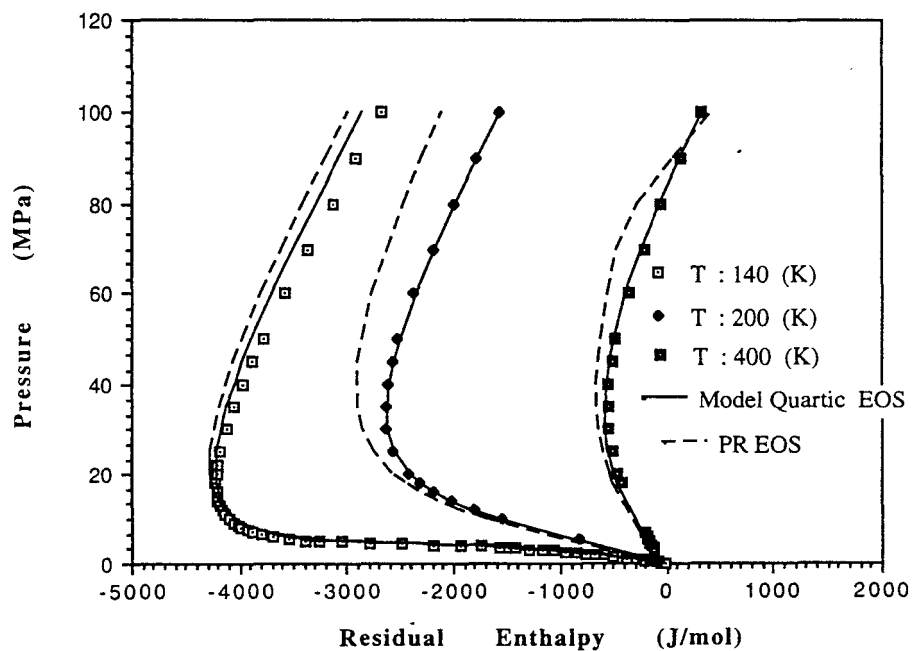


Figure 4.25: Comparison of residual enthalpy calculation for Carbon Monoxide using different equations of state

for the Peng-Robinson equation, respectively. Figure 4.25 compares the enthalpy departure calculations of carbon monoxide using two EOSs. To test the performance of two EOSs in low-pressure regions, 0.0-1.0 MPa, for enthalpy departure calculations, the comparisons for acetone and hydrogen sulfide have been presented in Figures 4.26 and 4.27, respectively. The AAD calculations for acetone and hydrogen sulfide were 2.86% and 1.82% for the generalized quartic equation, respectively; however, for the Peng-Robinson equation the results for these two compounds were 21.06% and 14.5%, respectively. The calculated values using the generalized quartic EOS compare very favorably with those calculated using the Peng-Robinson EOS for acetone and hydrogen sulfide. A comparison of the compressed liquid density calculation for Freon-11 (CCl_3F) using the two EOSs is reported in Figure 4.28. The AAD calculation for Freon-11 (CCl_3F) compressed liquid density was 1.42% for the generalized quartic equation and 5.29% for the Peng-Robinson equation. A good agreement between calculated and experimental data is still generated by the generalized quartic equation of state in Figure 4.28.

A summary of the average absolute deviation (AAD) calculations for seven physical and thermodynamic properties for 30 pure polar compounds obtained using the generalized quartic and Peng-Robinson equations of state is presented in Table 4.4. From the overall AAD calculations obtained, Table 4.4 shows that the overall performance of the quartic EOS is better than that of the Peng-Robinson EOS for pure polar fluid systems. The Peng-Robinson EOS

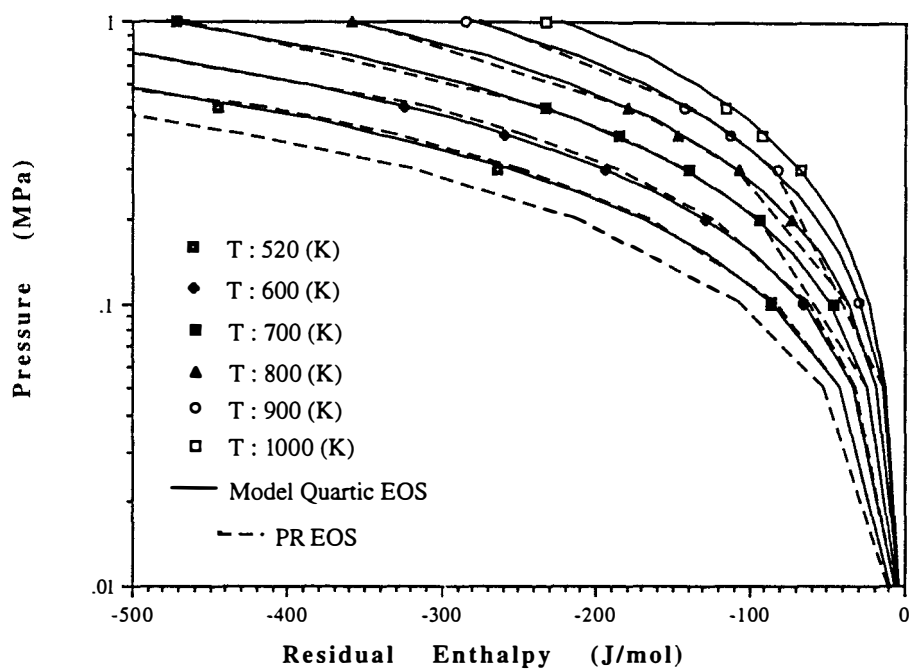


Figure 4.26: Comparison of residual enthalpy calculation for Acetone using different equations of state

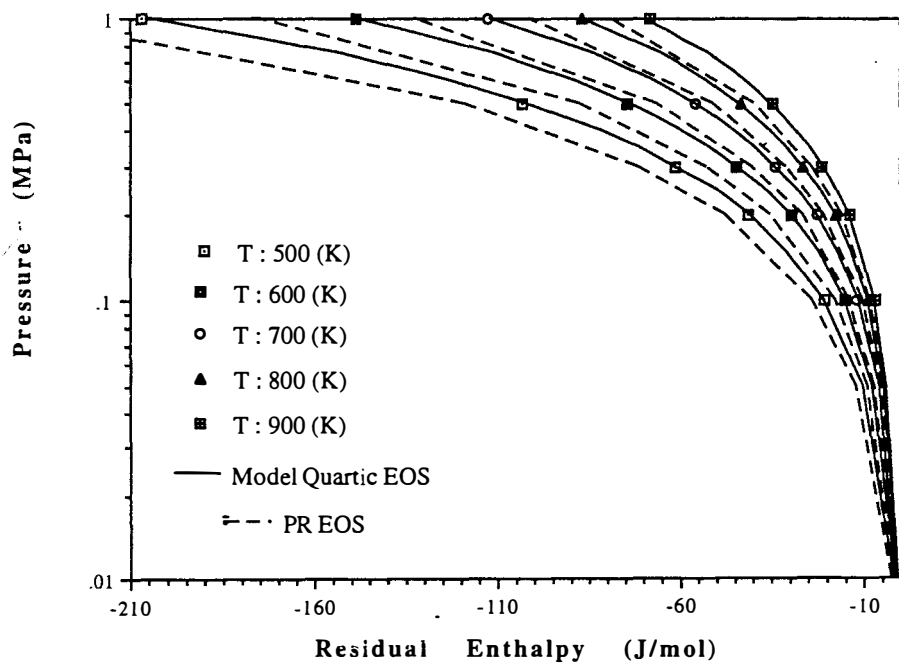


Figure 4.27: Comparison of residual enthalpy calculation for Hydrogen Sulfide using different equations of state

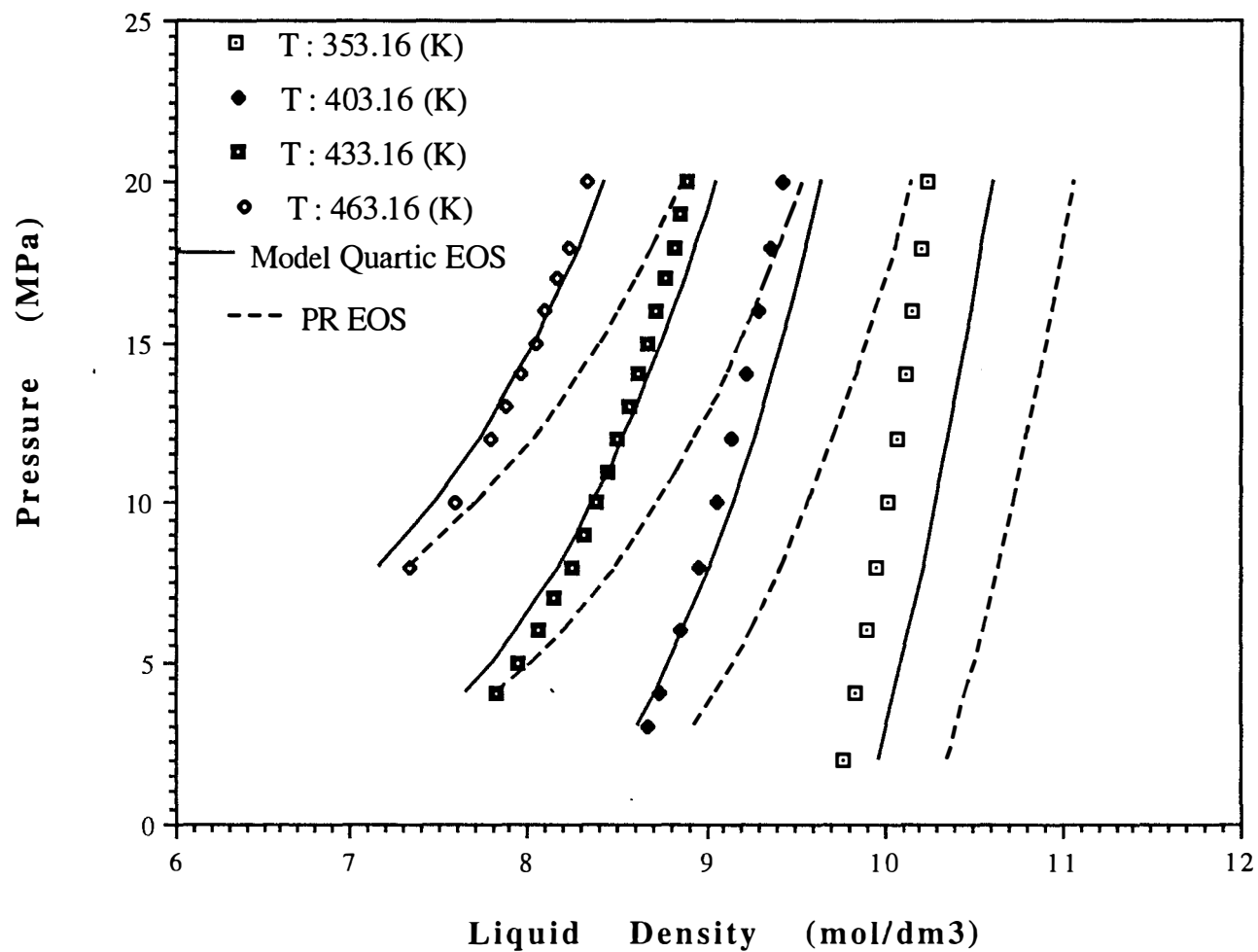


Figure 4.28: Comparison of compressed liquid density for Freon-11 (CCl_3F) using different equations of state

Table 4.4: Comparison of thermodynamic and physical properties for 30 polar compounds. AAD summary for the generalized quartic and Peng-Robinson equations of state

Thermodynamic and Physical Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	Number of Data Points
P_s	1.98	1.82	1456
ρ_{sv}	2.68	2.90	541
ρ_l	2.40	6.74	1586
ρ_g	0.89	2.08	2289
H_r	3.29	15.46	913
B_{vir}	1.71	57.05	609
H_v	1.91	1.82	1118

$$AAD(\%) = \frac{1}{N_d} \sum_{i=1}^{N_d} \left| \left(\frac{y_i^{\text{exp}} - y_i^{\text{calc}}}{y_i^{\text{exp}}} \right) \right| \times 100\%$$

(AAD = Average Absolute Deviation)

where

y^{exp} = the experimental data,

y^{calc} = the calculated data, and

N_d = the number of data points.

still performs slightly better than the generalized quartic EOS with regard to saturated vapor pressure and enthalpy of vaporization calculations. On the other hand, the generalized quartic EOS makes a significant improvement in calculating the enthalpy departure, second virial coefficients, and the pressure-volume-temperature properties.

A detailed description of the comparisons of the AAD calculations for seven physical and thermodynamic properties of 30 pure polar compounds using the generalized quartic and Peng-Robinson equations of state is given in Appendix C. In general, the generalized quartic EOS predicts more accurately than the Peng-Robinson EOS, especially in the supercritical and compressed liquid density regions.

To demonstrate the ability of the new generalized quartic EOS for nonpolar and polar fluids to represent polar systems, we arbitrarily chose seven pure polar substances, Freon-12 (CCl_2F_2), methyl ethyl ketone, m-xylene, toluene, ethylbenzene, 1H-pyrrole, and 1,1-difluoroethane, which were not included in the regressions for the data of 30 polar fluids. These seven polar fluids were examined using the new set of regressed coefficients in the generalized quartic EOS. The thermodynamic properties of seven pure polar compounds is given in Table 4.5. Their data ranges and data sources are presented in Table 4.6. The results of various thermodynamic property and density calculations for these

Table 4.5: Pure polar compound physical properties used in testing the ability of the generalized quartic equation of state

Compound	Critical Temperature (K)	Critical Volume (dm ³ /mol)	Acentric Factor	Dipole Moment (debye)	Data* Sources
Dichlorodifluoromethane (CCl ₂ F ₂)	384.95	0.217	0.1796	0.510	[1], [2], [4]
Methyl Ethyl Ketone	535.5	0.267	0.3241	2.760	[1]
m-Xylene	617.05	0.3758	0.3260	0.300	[1]
Ethylbenzene	617.17	0.37381	0.3036	0.590	[1]
Toluene	591.79	0.31579	0.2641	0.360	[1]
1H-Pyrrole	639.75	0.230	0.2876	1.840	[1]
1,1-difluoroethane	386.6	0.181	0.2629	2.270	[1], [2]

* Appendix E

Table 4.6: A description of seven polar fluid data ranges used and
their sources (* Appendix E)

Compound	Properties	Temperature Range (K)	Pressure Range(MPa)	No. of Data Points	Data Ref.*
Dichloro- difluoro- methane (CCl ₂ F ₂)	P _s	230-383	0-80 0-50	30	[4]
	ρ _{sv}	230-383		30	[4]
	ρ _{sl}	230-383		30	[4]
	ρ _g	390-470		72	[4]
	H _r	400-520		56	[2]
	B _{vir}	340-470		27	[1]
	H _v	230-365		26	[4]
Methyl Ethyl Ketone	P _s	200-530		34	[1]
	ρ _{sl}	200-530		34	[1]
	B _{vir}	850-1150		31	[1]
	H _v	200-510		32	[1]
m-Xylene	P _s	350-610		27	[1]
	ρ _{sl}	350-610		27	[1]
	H _v	350-590		25	[1]
Ethyl Benzene	P _s	290-610		17	[1]
	ρ _{sl}	290-610		17	[1]
	B _{vir}	550-800		26	[1]
	H _v	290-590		16	[1]
Toluene	P _s	250-590		35	[1]
	ρ _{sl}	250-590		35	[1]
	H _v	250-570		33	[1]
1,1- difluoro- ethane	P _s	160-385	0-75	24	[1]
	ρ _{sl}	160-385		24	[1]
	H _r	400-550		80	[2]
	H _v	160-360		21	[1]
1H-Pyrrole	P _s	320-630		32	[1]
	H _v	320-600		29	[1]

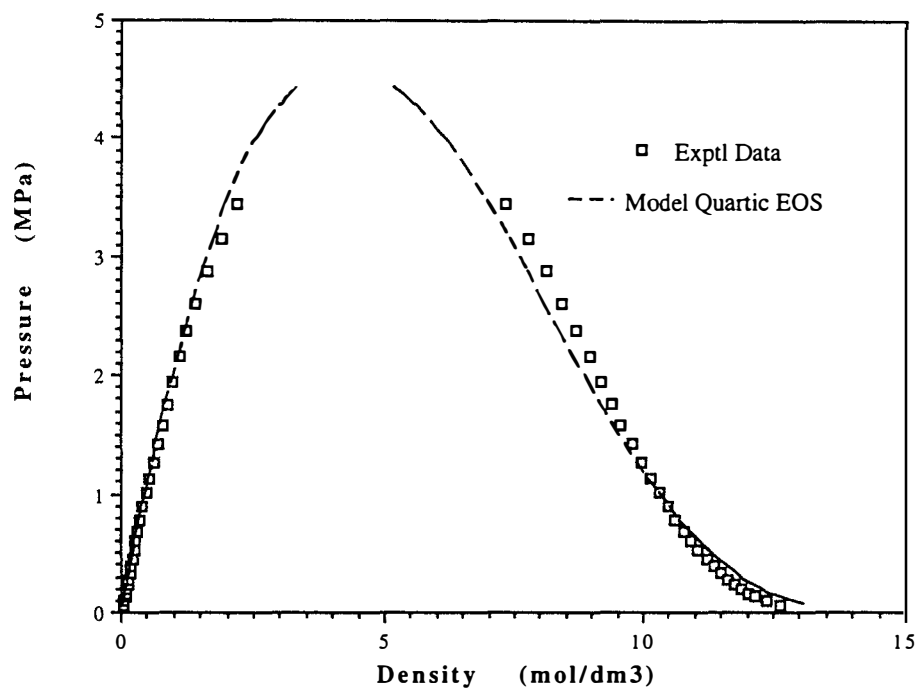


Figure 4.29: Saturated VLE calculation for Freon-12(CCl₂F₂)

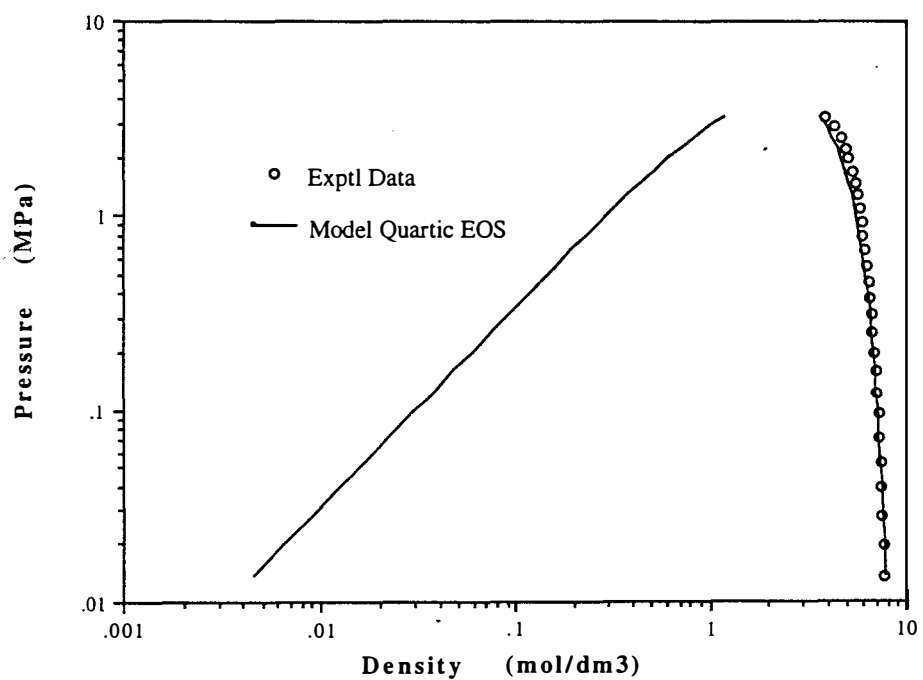


Figure 4.30: Saturated liquid density calculation for m-Xylene

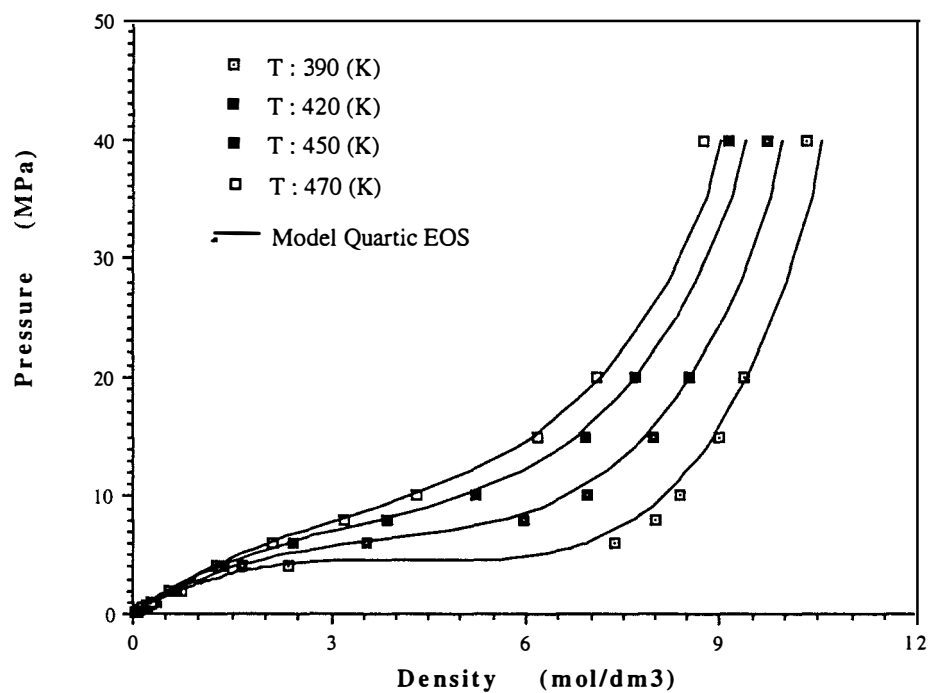


Figure 4.31: Pressure-density calculation for Freon-12 (CCl₂F₂)

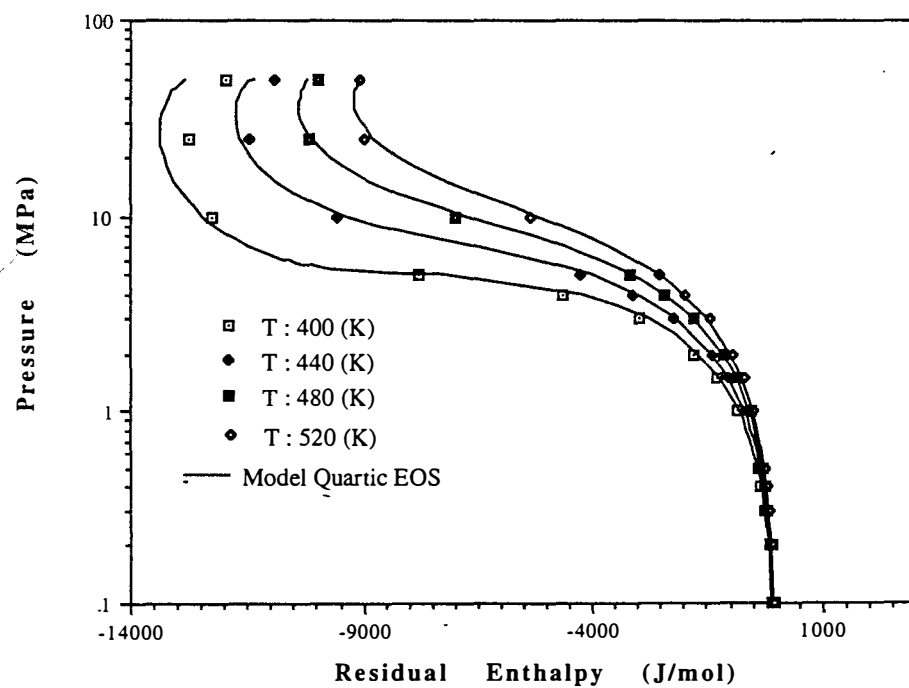


Figure 4.32: Residual enthalpy calculation for Freon-12 (CCl₂F₂)

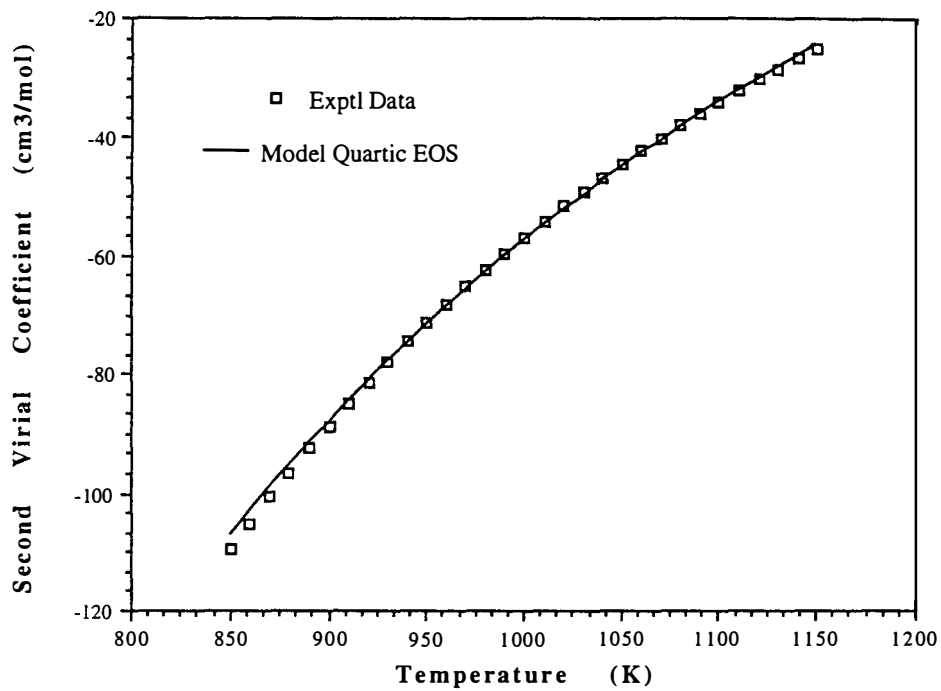


Figure 4.33: Second virial coefficient calculation for Methyl Ethyl Ketone

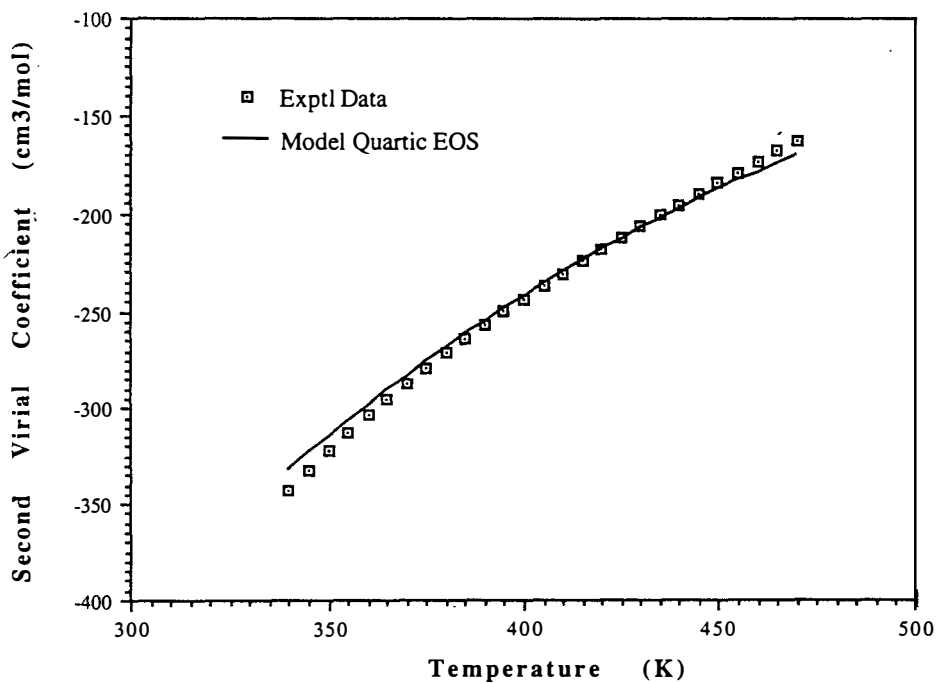


Figure 4.34: Second virial coefficient calculation for Freon-12

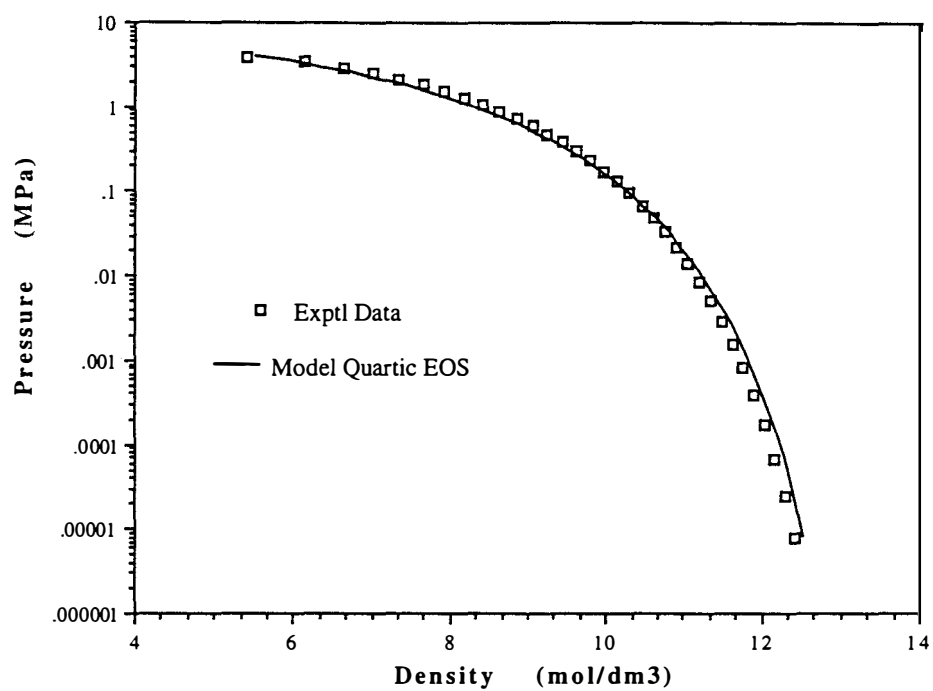


Figure 4.35: Saturated liquid density calculation for Methyl Ethyl Ketone

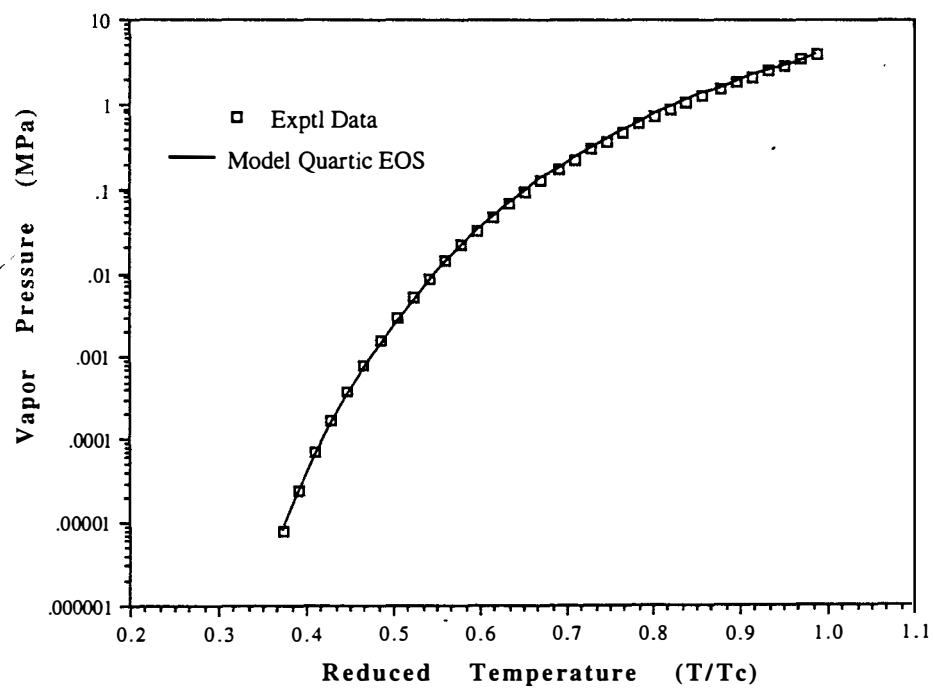


Figure 4.36: Vapor pressure calculation for Methyl Ethyl Ketone

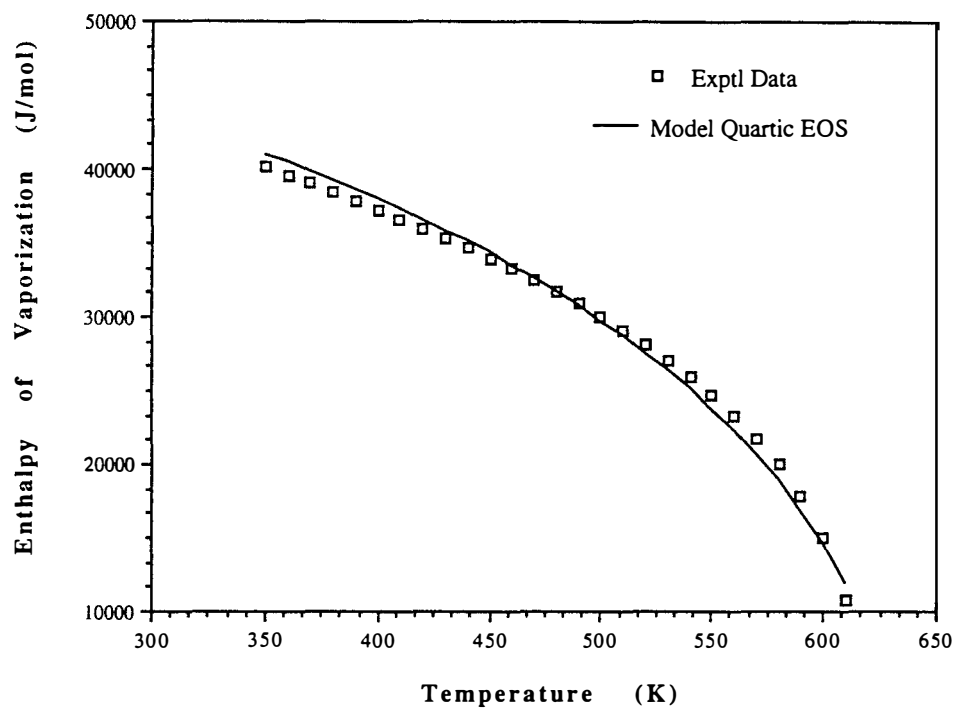


Figure 4.37: Enthalpy of vaporization calculation for m-Xylene

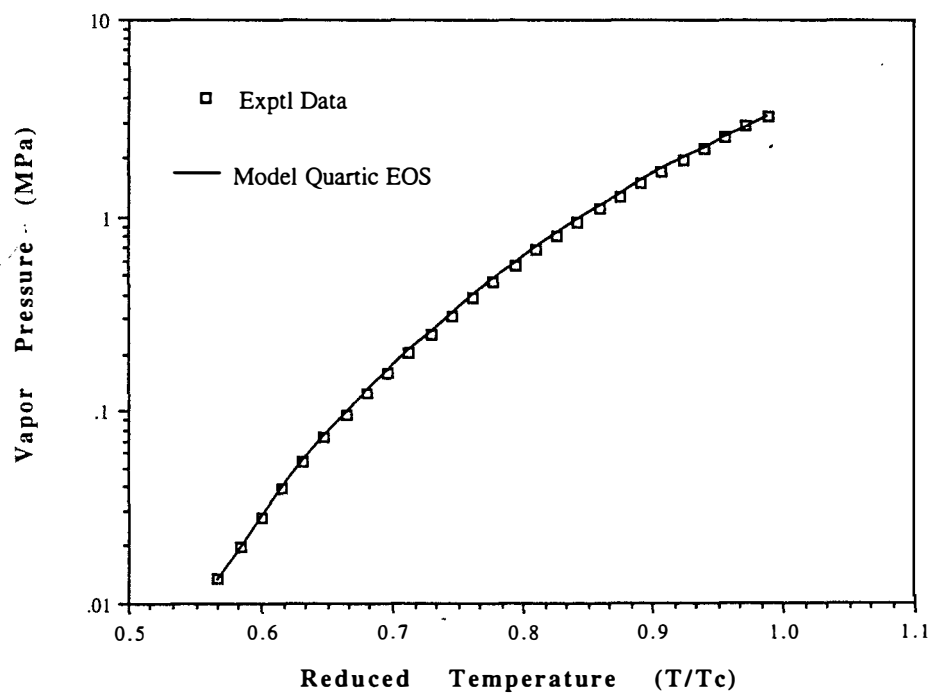


Figure 4.38: Vapor pressure calculation for m-Xylene

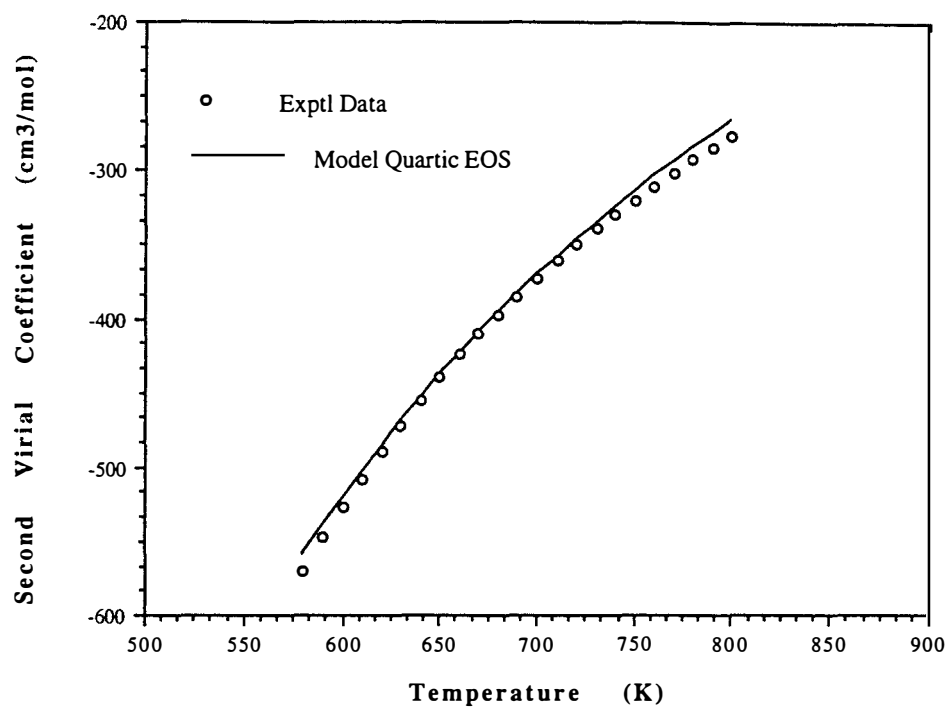


Figure 4.39: Second virial coefficient calculation for Ethylbenzene

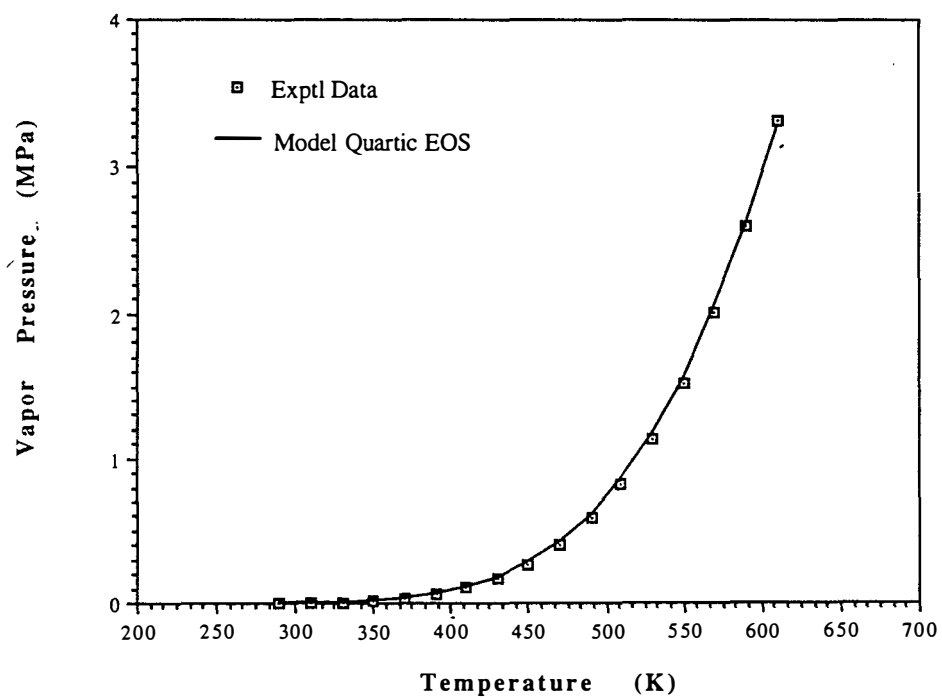


Figure 4.40: Vapor pressure calculation for Ethylbenzene

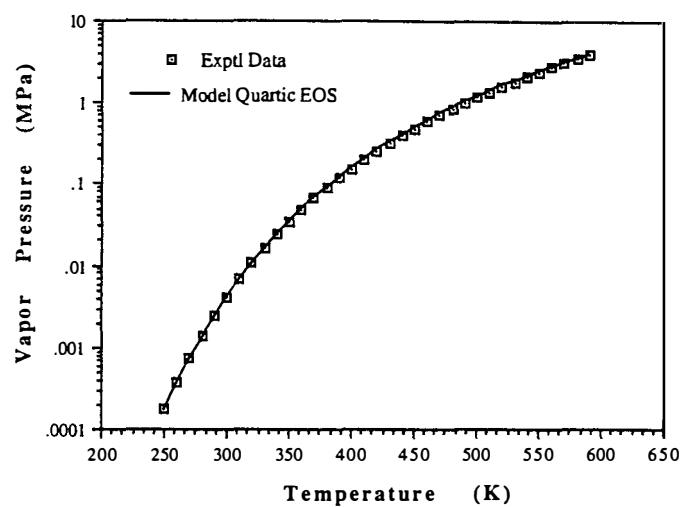


Figure 4.41: Vapor pressure calculation for Toluene

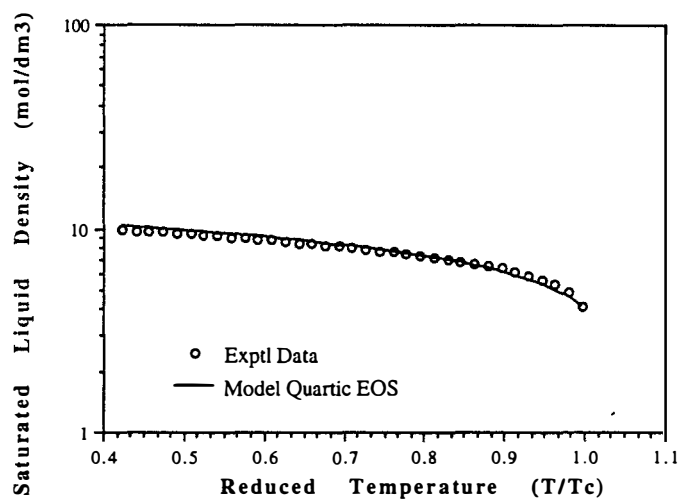


Figure 4.42: Saturated liquid density calculation for Toluene

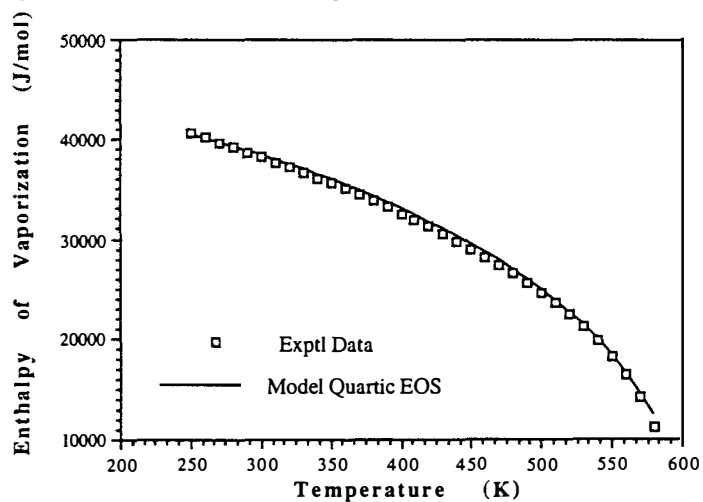


Figure 4.43: Enthalpy of vaporization calculation for Toluene

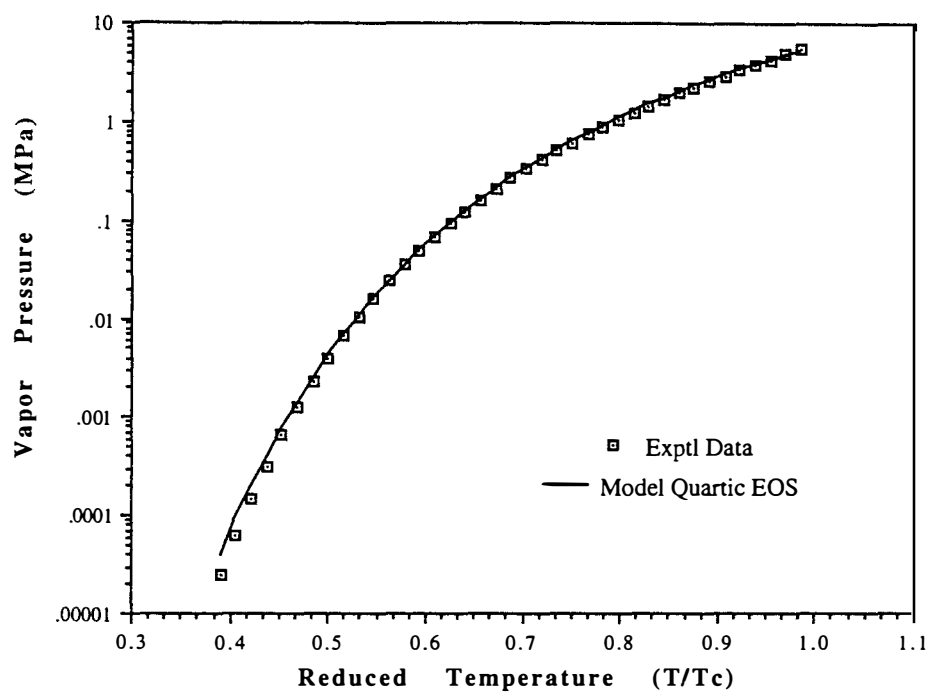


Figure 4.44: Vapor pressure calculation for 1H-Pyrrole

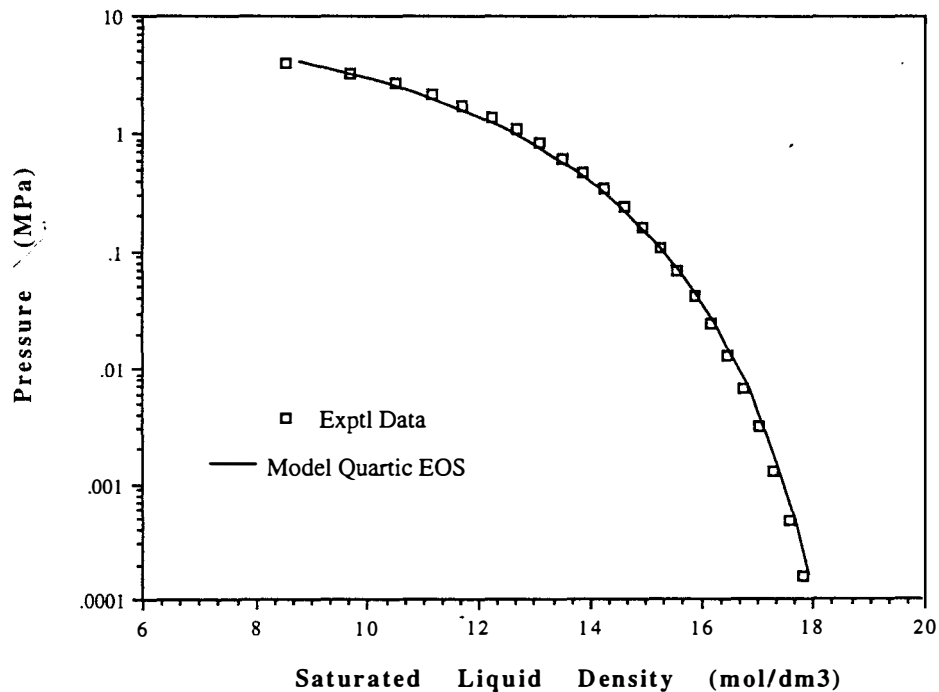


Figure 4.45: Saturated liquid density calculation for 1,1-Difluoroethane

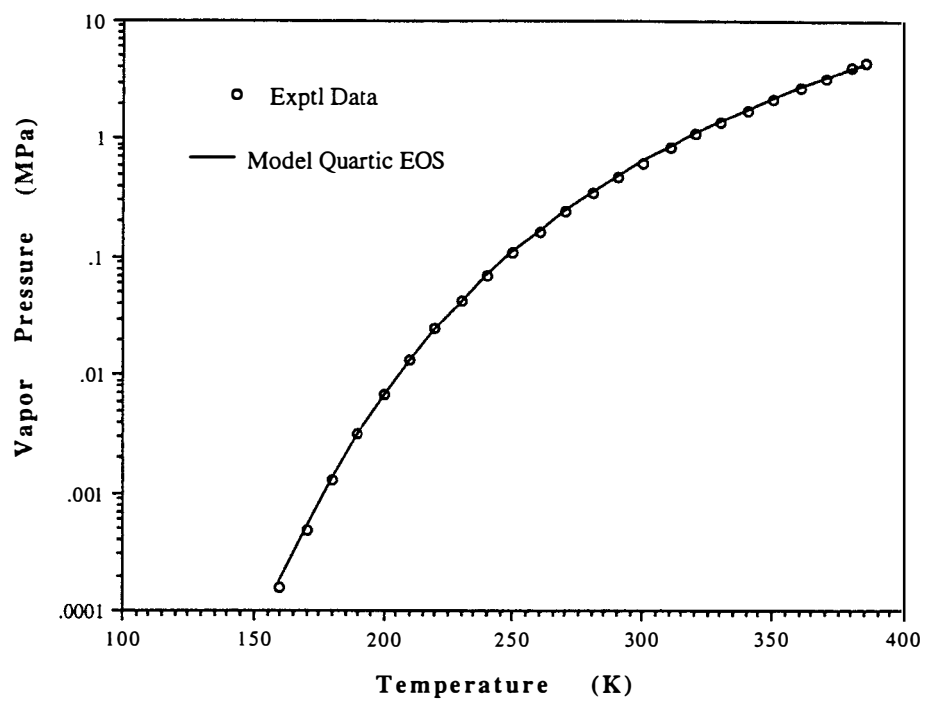


Figure 4.46: Vapor pressure calculation for 1,1-Difluoroethane

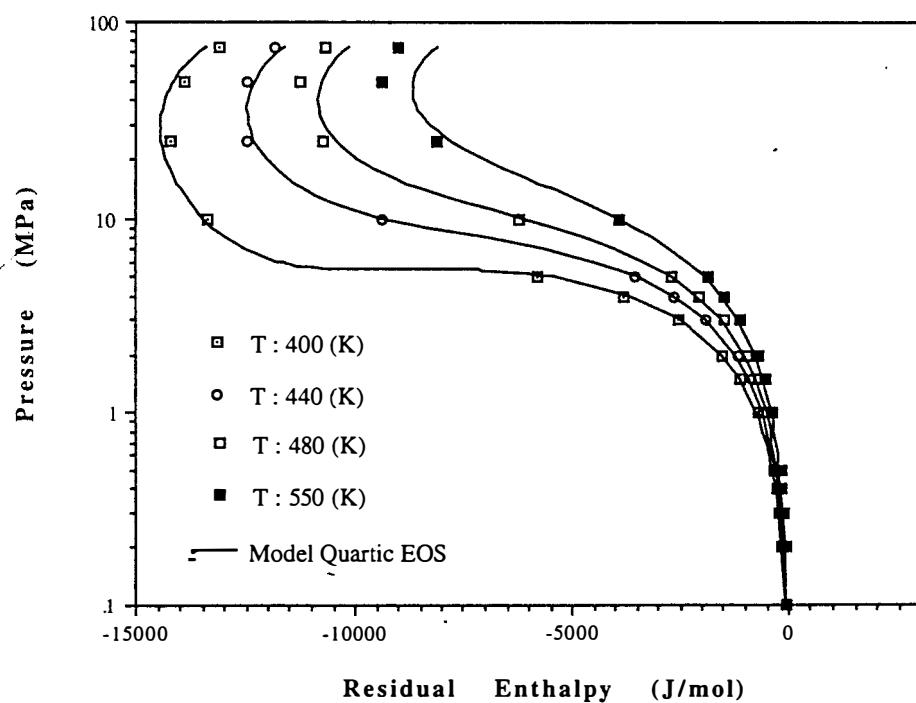


Figure 4.47: Residual enthalpy calculation for 1,1-Difluoroethane

Table 4.7: AAD of various thermodynamic properties for seven polar fluids using the generalized quartic and PR equations of state

Compound	Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	No. of Data Points
Dichlorodifluoromethane (CCl ₂ F ₂)	P _s	1.14	0.52	30
	ρ _{sv}	2.78	1.57	30
	ρ _{sl}	2.42	5.60	30
	ρ _g	1.17	2.45	72
	H _r	2.87	11.59	56
	B _{vir}	1.45	12.75	27
	H _v	2.41	1.07	26
Methyl Ethyl Ketone	P _s	4.45	2.33	34
	ρ _{sl}	1.44	9.64	34
	B _{vir}	0.92	35.04	31
	H _v	2.85	1.47	32
m-Xylene	P _s	2.16	0.31	27
	ρ _{sl}	3.44	5.33	27
	H _v	2.18	2.14	25
Ethyl- Benzene	P _s	2.50	1.33	17
	ρ _{sl}	2.88	3.58	17
	B _{vir}	1.43	7.42	26
	H _v	1.36	1.63	16
Toluene	P _s	2.73	2.07	35
	ρ _{sl}	3.02	2.99	35
	H _v	1.25	1.84	33
1,1- difluoro- ethane	P _s	2.03	1.41	24
	ρ _{sl}	1.48	9.63	24
	H _r	4.62	21.10	80
	H _v	3.37	1.16	21
1H-Pyrrole	P _s	1.76	2.76	32
	H _v	1.87	2.77	29

compounds are shown in Figures 4.29-4.47. Table 4.7 shows the AAD calculations of various thermodynamic properties for the generalized quartic and Peng-Robinson equations for each of seven polar compounds not used in the regressions. A summary of the overall performance for the generalized quartic and Peng-Robinson equations for seven polar compounds is reported in Table 4.8. Various thermodynamic properties predicted from the generalized quartic EOS are in reasonable agreement with the experimental data. These results show that the capability of the new set of regressed coefficients is generally applicable to various thermodynamic properties and densities of pure polar compounds.

From all results presented in this chapter, the new set of regressed coefficients has been reliably determined using the effective regression technique. Therefore, as for the entire homogeneous fluid region, the generalized quartic EOS has achieved higher precision compared with the traditional and widely used Peng-Robinson EOS.

Table 4.8: Comparison of thermodynamic and physical properties for seven polar compounds. AAD summary for the generalized quartic and Peng-Robinson equations of state

Thermodynamic and Physical Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	Number of Data Points
P_s	2.45	1.61	199
ρ_{sv}	2.78	1.57	30
ρ_{sl}	2.43	6.20	167
ρ_g	1.17	2.45	72
H_r	3.90	17.18	136
B_{vir}	1.25	19.33	84
H_v	2.18	1.76	182

$$AAD(\%) = \frac{1}{N_d} \sum_{i=1}^{N_d} \left| \left(\frac{y_i^{\text{exp}} - y_i^{\text{calc}}}{y_i^{\text{exp}}} \right) \right| \times 100\%$$

(AAD = Average Absolute Deviation)

where

y^{exp} = the experimental data,

y^{calc} = the calculated data, and

N_d = the number of data points.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

A quartic EOS, previously developed and generalized for nonpolar fluids, has been extended and generalized for polar fluids as well. A new set of regressed coefficients in the generalized quartic EOS has been presented using nonlinear regressions for 30 polar fluids. This set of regressed coefficients is applicable to the thermodynamic property calculations for nonpolar and polar fluids. In order to evaluate the thermodynamic properties of the fluid, this EOS is only characterized by four properties of the fluid, the critical temperature, the critical volume, the acentric factor, and the dipole moment. Thus, with its simplicity and capability, the generalized quartic EOS has been developed which accurately offers a good representation of the physical and thermodynamic properties for pure polar fluids. Satisfactory results have been obtained for the tested polar compounds, and a significant improvement over the Peng-Robinson EOS has been made for pure polar fluids.

The generalized quartic EOS is as capable of predicting the saturation VLE values as is the traditional cubic equation of state. A deliberate decision was made to sacrifice accuracy of this EOS near critical point in order to achieve greater accuracy for a wide range of properties over a wide range of states. Consequently, this equation is

not as accurate as the traditional cubic equations of state near the critical point. Although it produces larger errors in pressure-density calculations in the critical region, on the whole, it yields higher accuracy in calculating the saturated liquid and vapor volume for pure polar fluids. It also performs well when temperatures reach to 1000 °C and pressures reach 100 MPa. In addition, its performance improves significantly in the supercritical and compressed liquid density regions. Therefore, by taking into consideration the dipole moment for pure polar fluids, the generalized quartic equation of state performs remarkably better than the well-known Peng-Robinson EOS.

The results of this research lead to some recommendations for further study and development.

1. A test of the generalized quartic EOS using the new set of regressed coefficients should be extended to a great number of nonpolar and polar fluids that were not included in the regressions.

2. To strengthen the capability and accuracy of the generalized quartic EOS for use with polar fluids, besides the dipole moment of the fluid, the other multipole moments should be considered for use in the equation of state.

3. At low reduced temperatures, the generalized quartic EOS produces large deviations from the experimental data. For future

work, a modification of the functional form of $\alpha(T_r)$ is suggested to improve second virial coefficient calculations at the subcritical region.

4. Extended work is being undertaken to pursue a systematic approach to the development of the generalized quartic EOS that can represent adequately the properties of vapor and liquid mixtures including polar fluids. Boublik and Mansoori extended the Carnahan-Starling equation to a mixture of hard-spheres. A comparison of the Boublik-Mansoori (BM) method with the traditional vdW one fluid theory was made by Dimitrelis and Prausnitz (1986). Using the generalized quartic equation for mixtures, Shah (1992) proposed that the BM reference system is superior to vdW one fluid reference system. Hence, based on the studies of Shah (1992), the BM method should be used for the repulsive pressure term and the vdW one fluid mixing rules should be used for the parameters a , c , and e , while testing mixtures using the quartic equation.

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APPENDIXES

APPENDIX A

Determining the Regressed Coefficients for Polar Fluids Using Computer Programs

A Procedure for Determining the Regressed Coefficients for Polar Fluids Using Computer Programs

1. Establish a database using extensive experimental data for 30 pure polar fluids.
2. Start running programs from the smallest value of a reduced dipole moment of a polar compound and use its physical and thermodynamic property data to evaluate regressed coefficients.
3. For the saturated-phase region, the saturation experimental data, such as the vapor pressure, the saturated liquid and vapor densities, and enthalpy of vaporization are initially used close to $0.9T_c$.
4. Give a set of arbitrary coefficients corresponding to μ^* and μ^{*2} .
5. Locate the minimum value of the objective function, i.e., find the smallest average absolute deviation for each physical property and the smallest sum of squares of residual.
6. If not converging to a minimum value, change a new set of regressed coefficients again until the values of item 5 approach a minimum.

7. Then take the final coefficients determined from the program running for the first compound as the second set of initial coefficients while adding the second compound.
8. Similarly, following the same step as described in item 7, then repeat this procedure for the rest of compounds.
9. Take the final set of regressed coefficients from the result of item 8, begin adding the first compound's saturation data as close to its critical region as possible, and repeat the step in item 7 until reaching the final compound.
10. Using the final optimum regressed coefficients obtained, plus previously reported coefficients which are kept constant during regressions, specify the quartic equation of state for nonpolar and polar fluids.

APPENDIX B

Pure Polar Fluid Data Used in the Regressions and Their Data Sources

Table B.1: A detailed description of the pure component data used in regressions and their sources. (* Appendix E)

Compound	Properties	Temperature Range (K)	Pressure Range(MPa)	No. of Data Points	Data Ref.*
Acetone	P_s	400-505	0-100	31	[1]
	ρ_{sl}	400-505		31	[1]
	H_r	520-1000		110	[1]
	B_{vir}	600-700		30	[2]
	H_v	320-475		41	[1]
Carbon Monoxide	P_s	80-132	0-100	45	[3]
	ρ_{sv}	80-132		45	[3]
	ρ_{sl}	80-132		45	[3]
	ρ_g	140-1000		559	[3]
	H_r	140-400		104	[3]
	B_{vir}	140-360		41	[3]
	H_v	68-128		31	[3]
Carbonyl Sulfide	P_s	180-375		39	[1]
	ρ_{sl}	180-375		39	[1]
	B_{vir}	460-680		53	[1]
	H_v	150-360		43	[1]
Methyl Acetate	P_s	270-505		62	[1]
	ρ_{sl}	270-505		62	[1]
	H_v	250-480		42	[1]
Ethyl Acetate	P_s	250-520		63	[1]
	ρ_{sl}	250-520		63	[1]
	B_{vir}	530-650		35	[1]
	H_v	253-503		26	[1]
n-Propyl Acetate	P_s	260-540		71	[1]
	ρ_{sl}	260-540		71	[1]
	B_{vir}	530-620		32	[1]
	H_v	300-530		47	[1]
n-Butyl Acetate	P_s	360-570		61	[1]
	ρ_{sl}	360-570		61	[1]
	B_{vir}	580-750		36	[1]
	H_v	300-565		50	[1]

Table B.1 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range(MPa)	No. of Data Points	Data Ref.*
Freon-11 (CCl ₃ F)	P _s	225-470		76	[4]
	ρ _{sv}	225-470		76	[4]
	ρ _{sl}	225-470		76	[4]
	ρ _l	353.15-463.15	0-20	47	[4]
	H _r	480-1000	0-50	84	[2]
	H _v	220-455		58	[1]
Freon-13 (CClF ₃)	P _s	180-295		40	[4]
	ρ _{sv}	180-295		40	[4]
	ρ _{sl}	180-295		40	[4]
	ρ _g	310-450	0-50	46	[4]
	H _r	340-1000	0-50	85	[2]
	H _v	150-290		29	[4]
Freon-21 (CHFCl ₂)	P _s	250-450		53	[4]
	ρ _{sv}	250-450		53	[4]
	ρ _{sl}	250-450		53	[4]
	ρ _g	460-470	0-90	31	[4]
	ρ _l	320-450	1-90	52	[4]
	H _r	600-1000	0-50	65	[2]
	H _v	250-435		36	[4]
Freon-22 (CHClF ₂)	P _s	233.15-361.15		49	[5]
	ρ _{sv}	233.15-361.15		49	[5]
	ρ _{sl}	233.15-361.15		49	[5]
	ρ _g	370-560	0-35	94	[4,6]
	H _r	420-800	0-100	65	[2]
	H _v	180-340		47	[4]

Table B.1 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range(MPa)	No. of Data Points	Data Ref.*
Freon-23 (CHF_3)	P_s	145-290	0-58 0-100	41	[4]
	ρ_{sv}	145-290		41	[4]
	ρ_{sl}	145-290		41	[4]
	ρ_g	300-470		89	[4]
	H_r	320-600		75	[2]
	B_{vir}	300-550		48	[1]
	H_v	145-275		39	[4]
Freon-114 ($\text{C}_2\text{Cl}_2\text{F}_4$)	P_s	250-410	0-20 1-20 0-100	44	[4]
	ρ_{sv}	250-410		44	[4]
	ρ_{sl}	250-410		44	[4]
	ρ_g	420-500		74	[4]
	ρ_l	300-400		31	[4]
	H_r	450-600		47	[2]
	H_v	250-395		42	[4]
Methyl Chloride	P_s	225-410	0-35	45	[8]
	ρ_{sv}	225-410		45	[8]
	ρ_{sl}	225-410		45	[8]
	ρ_g	473-623		98	[7]
	B_{vir}	480-600		37	[1]
	H_v	206-386		34	[1]
Methyl Fluoride	P_s	152.7-315		55	[1]
	ρ_{sl}	152.7-315		55	[1]
	B_{vir}	700-950		61	[1]
	H_v	167.7-282.7		33	[1]
Ethyl Chloride	P_s	200-450		50	[1]
	ρ_{sl}	200-450		50	[1]
	H_v	200-435		43	[1]
Chloroform	P_s	250-514		32	[1]
	ρ_{sl}	250-514		32	[1]
	H_v	250-510		53	[1]

Table B.1 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range(MPa)	No. of Data Points	Data Ref.*
Chlorobenzene	P_s	353-630	0-100	58	[1]
	ρ_{sl}	353-630		58	[1]
	H_r	650-900		78	[2]
	B_{vir}	670-900		62	[1]
	H_v	355-605		46	[1]
Dimethyl Ether	P_s	230-396		57	[1]
	ρ_{sl}	230-396		57	[1]
	H_v	180-375		40	[1]
Diethyl Ether	P_s	260-463	0-100	36	[1]
	ρ_{sl}	260-463		36	[1]
	H_r	480-600		35	[2]
	H_v	255-445		39	[1]
Methyl Ethyl Ether	P_s	320-435		48	[1]
	ρ_{sl}	320-435		48	[1]
	H_v	320-370		19	[1]
Hydrogen Bromide	P_s	250-360		42	[1]
	ρ_{sl}	250-360		42	[1]
	H_v	200-335		32	[1]
Hydrogen Iodide	P_s	300-420		47	[1]
	ρ_{sl}	300-420		47	[1]
	H_v	230-390		41	[1]
Water	P_s	273.16-633.16	0-100	60	[9]
	ρ_{sv}	273.16-633.16		60	[9]
	ρ_{sl}	273.16-633.16		60	[9]
	ρ_g	773.16-1273.16	0-100	417	[9]
	B_{vir}	660-780		37	[1]
	H_r	900-1100		48	[6]
	H_v	300-600		38	[1]

Table B.1 (cont'd)

Compound	Properties	Temperature Range (K)	Pressure Range(MPa)	No. of Data Points	Data Ref.*
Hydrogen Sulfide	P_s	250-366	20-170 0-50	54	[1]
	ρ_{sl}	250-366		54	[1]
	ρ_g	453-493		48	[10]
	H_r	500-900		43	[2]
	H_v	200-355		43	[1]
Methanol	P_s	300-500	0-70	24	[11]
	ρ_{sv}	300-500		24	[11]
	ρ_{sl}	300-500		24	[11]
	ρ_g	640-800		103	[11]
	H_v	400-495		33	[1]
Ammonia	P_s	200.15-395.15	0-100	64	[12]
	ρ_{sv}	200.15-395.15		64	[12]
	ρ_{sl}	200.15-395.15		64	[12]
	ρ_g	450-800		312	[12]
	H_v	200-360		38	[1]
Nitrous Oxide	P_s	230-305	0-32	62	[1]
	ρ_{sl}	230-305		62	[1]
	ρ_g	323.16-423.16		119	[13]
	B_{vir}	315-520		53	[1]
	H_v	190-295		22	[1]
Sulfur Dioxide	P_s	270-425	0-32 0-100	47	[1]
	ρ_{sl}	270-425		47	[1]
	ρ_g	430-523		299	[14]
	H_r	450-900		74	[2]
	B_{vir}	440-550		39	[1]
	H_v	205-395		33	[1]
Acrylonitrile	B_{vir}	810-970		45	[1]

APPENDIX C

Average Absolute Deviation of Thermodynamic and Physical Properties Using Different Equations of State

Table C.1: AAD's calculations using different equations of state

Compound	Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	No. of Data Points
Acetone	P_s	4.85	0.48	31
	ρ_{sl}	3.41	21.95	31
	H_r	2.86	21.06	110
	B_{vir}	1.96	20.62	30
	H_v	2.15	0.53	41
Carbon Monoxide	P_s	2.49	3.42	45
	ρ_{sv}	2.25	6.26	45
	ρ_{sl}	2.47	8.67	45
	ρ_g	0.73	1.94	559
	H_r	3.17	16.01	104
	B_{vir}	1.11	196.11	41
	H_v	2.76	3.21	31
Carbonyl Sulfide	P_s	2.72	1.10	39
	ρ_{sl}	6.42	6.76	39
	B_{vir}	1.72	20.57	53
	H_v	1.26	2.23	43
Methyl Acetate	P_s	2.13	1.14	62
	ρ_{sl}	1.73	5.74	62
	H_v	1.91	1.46	42
Ethyl Acetate	P_s	1.50	3.93	63
	ρ_{sl}	3.34	8.96	63
	B_{vir}	1.22	7.00	35
	H_v	0.82	1.76	26
n-Propyl Acetate	P_s	1.11	3.18	71
	ρ_{sl}	1.46	5.35	71
	B_{vir}	1.97	7.18	32
	H_v	0.81	1.53	47
n-Butyl Acetate	P_s	1.65	0.65	61
	ρ_{sl}	2.59	4.45	61
	B_{vir}	1.81	3.37	36
	H_v	1.07	1.62	50

Table C.1 (cont'd)

Compound	Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	No. of Data Points
Freon-11 (CCl ₃ F)	P _s	1.75	1.78	76
	ρ _{sv}	1.89	2.06	76
	ρ _{sl}	2.80	5.28	76
	ρ _l	1.42	5.29	47
	H _r	2.94	12.02	84
	H _v	1.32	2.00	58
Freon-13 (CClF ₃)	P _s	1.14	0.87	40
	ρ _{sv}	2.30	1.16	40
	ρ _{sl}	2.33	6.54	40
	ρ _g	1.04	2.33	46
	H _r	3.42	12.66	85
	H _v	2.82	1.00	29
Freon-21 (CHFC1 ₂)	P _s	1.99	0.91	53
	ρ _{sv}	1.94	1.74	53
	ρ _{sl}	2.65	4.03	53
	ρ _g	1.63	3.18	31
	ρ _l	2.90	4.72	52
	H _r	2.36	14.96	65
	H _v	2.41	0.99	36
Freon-22 (CHClF ₂)	P _s	0.99	0.34	49
	ρ _{sv}	3.21	1.19	49
	ρ _{sl}	1.63	2.93	49
	ρ _g	0.35	1.15	94
	H _r	3.30	14.83	65
	H _v	2.13	1.62	47

Table C.1 (cont'd)

Compound	Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	No. of Data Points
Freon-23 (CHF ₃)	P _s	1.98	0.49	41
	ρ _{sv}	4.54	1.64	41
	ρ _{sl}	0.46	5.00	41
	ρ _l	0.77	1.61	89
	H _r	5.02	18.68	75
	B _{vir}	1.75	7.51	48
	H _v	2.92	1.35	39
Freon-114 (C ₂ Cl ₂ F ₄)	P _s	0.66	0.30	44
	ρ _{sv}	1.66	0.97	44
	ρ _{sl}	2.21	4.04	44
	ρ _g	0.62	1.50	74
	ρ _l	2.31	5.65	31
	H _r	3.67	12.57	47
	H _v	1.04	0.67	42
Methyl Chloride	P _s	0.66	1.84	45
	ρ _{sv}	2.94	2.00	45
	ρ _{sl}	2.07	2.43	45
	ρ _g	0.79	1.90	98
	B _{vir}	1.91	16.99	37
	H _v	2.10	0.82	34
Methyl Fluoride	P _s	1.70	2.70	55
	ρ _{sl}	2.63	12.50	55
	B _{vir}	1.79	330.01	61
	H _v	2.25	1.39	33
Ethyl Chloride	P _s	1.86	2.20	50
	ρ _{sl}	2.16	6.22	50
	H _v	1.74	1.93	43
Chloroform	P _s	4.86	1.97	32
	ρ _{sl}	2.37	6.28	32
	H _v	0.78	2.26	53

Table C.1 (cont'd)

Compound	Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	No. of Data Points
Chlorobenz- ene	P_s	2.35	3.65	58
	ρ_{sl}	2.24	2.99	58
	H_r	3.41	12.81	78
	B_{vir}	1.13	15.76	62
	H_v	2.19	1.02	46
Dimethyl Ether	P_s	0.88	0.50	57
	ρ_{sl}	2.30	4.29	57
	H_v	3.13	0.53	40
Diethyl Ether	P_s	2.15	0.81	36
	ρ_{sl}	2.54	2.99	36
	H_r	2.12	12.75	35
	H_v	1.62	1.64	39
Methyl Ethyl Ether	P_s	2.32	1.45	48
	ρ_{sl}	2.25	6.44	48
	H_v	1.85	2.48	19
Hydrogen Bromide	P_s	0.72	1.04	42
	ρ_{sl}	2.19	5.63	42
	H_v	1.77	2.13	32
Hydrogen Iodide	P_s	1.89	0.27	47
	ρ_{sl}	1.80	5.63	47
	H_v	1.24	1.71	41
Water	P_s	3.33	6.60	60
	ρ_{sv}	2.86	7.50	60
	ρ_{sl}	3.50	17.59	60
	ρ_g	0.38	1.48	417
	B_{vir}	2.28	20.79	37
	H_r	4.97	20.63	48
	H_v	3.24	3.83	38

Table C.1 (cont'd)

Compound	Properties	Generalized Quartic EOS AAD (%)	Peng-Robinson EOS AAD (%)	No. of Data Points
Hydrogen Sulfide	P_s	1.01	1.24	54
	ρ_{sl}	1.99	5.39	54
	ρ_l	1.10	3.45	48
	H_r	1.82	14.50	43
	H_v	2.04	3.27	43
Methanol	P_s	3.96	2.51	24
	ρ_{sv}	3.44	5.23	24
	ρ_{sl}	5.48	15.57	24
	ρ_g	3.01	3.49	103
	H_v	2.09	5.07	33
Ammonia	P_s	3.38	2.17	64
	ρ_{sv}	3.24	2.48	64
	ρ_{sl}	0.72	11.86	64
	ρ_g	0.76	1.56	312
	H_v	2.25	1.62	38
Nitrous Oxide	P_s	2.54	0.61	62
	ρ_{sl}	2.69	8.11	62
	ρ_g	1.61	1.73	119
	B_{vir}	1.64	16.24	53
	H_v	2.74	2.52	22
Sulfur Dioxide	P_s	1.75	1.92	47
	ρ_{sl}	1.66	1.89	47
	ρ_g	1.22	3.66	299
	H_r	3.34	14.28	74
	B_{vir}	1.42	13.18	39
	H_v	2.71	1.59	33
Acrylonitrile	B_{vir}	2.55	3.54	45

APPENDIX D

The Calculation of Pure Fluid Phase Equilibrium

The Calculation of Pure Fluid Phase Equilibrium

The critical points of some pure polar fluids calculated using the new set of regressed coefficients are presented in Table D.1. These calculated values are obtained by using the criterion of phase equilibrium, the equality of the vapor and liquid fugacities in the coexisting phases. The algorithm to locate these values using the generalized quartic equation of state is shown in a flow diagram, Figure D.1. The critical temperature obtained using the generalized quartic equation of state is approximately 3.3% larger than the true critical temperature of the fluid.

Table D.1: Pure polar compound critical properties calculated using the generalized quartic equation of state

Compound	Critical Pressure		Critical Temperature		Critical Density	
	MPa	Error %	K	Error %	mol/dm ³	Error %
Methyl Chloride	6.793	12.98	416.25	2.58	7.194	-4.03
Chlorobenzene	4.5191	8.09	632.35	1.21	3.247	-8.23
Fluoroform	4.8362	13.48	298.89	2.71	7.502	-6.96
Water	22.055	23.95	647.13	3.24	17.873	-9.17
Hydrogen Sulfide	8.9629	8.35	373.53	1.46	10.153	-4.34
Methanol	8.0972	6.43	512.58	2.07	8.399	-21.34
Ammonia	11.278	23.96	405.65	3.04	13.799	-6.44
Carbon Monoxide	3.4988	2.47	132.92	0.81	10.741	-5.65
Freon-11 (CCl ₃ F)	4.4076	3.60	471.2	0.81	4.032	-7.02
Freon-22 (CHClF ₂)	4.971	11.31	369.3	1.95	6.024	-6.89
Sulfur Dioxide	7.8841	9.35	430.75	2.17	8.197	-6.71
n-Propyl Acetate	3.360	6.90	549.4	1.69	2.899	-14.34

$$Error(\%) = \left(\frac{C^{calc} - C^{exp}}{C^{exp}} \right) \times 100\%$$

where

C^{calc} = the calculated critical property,

C^{exp} = the experimental critical property

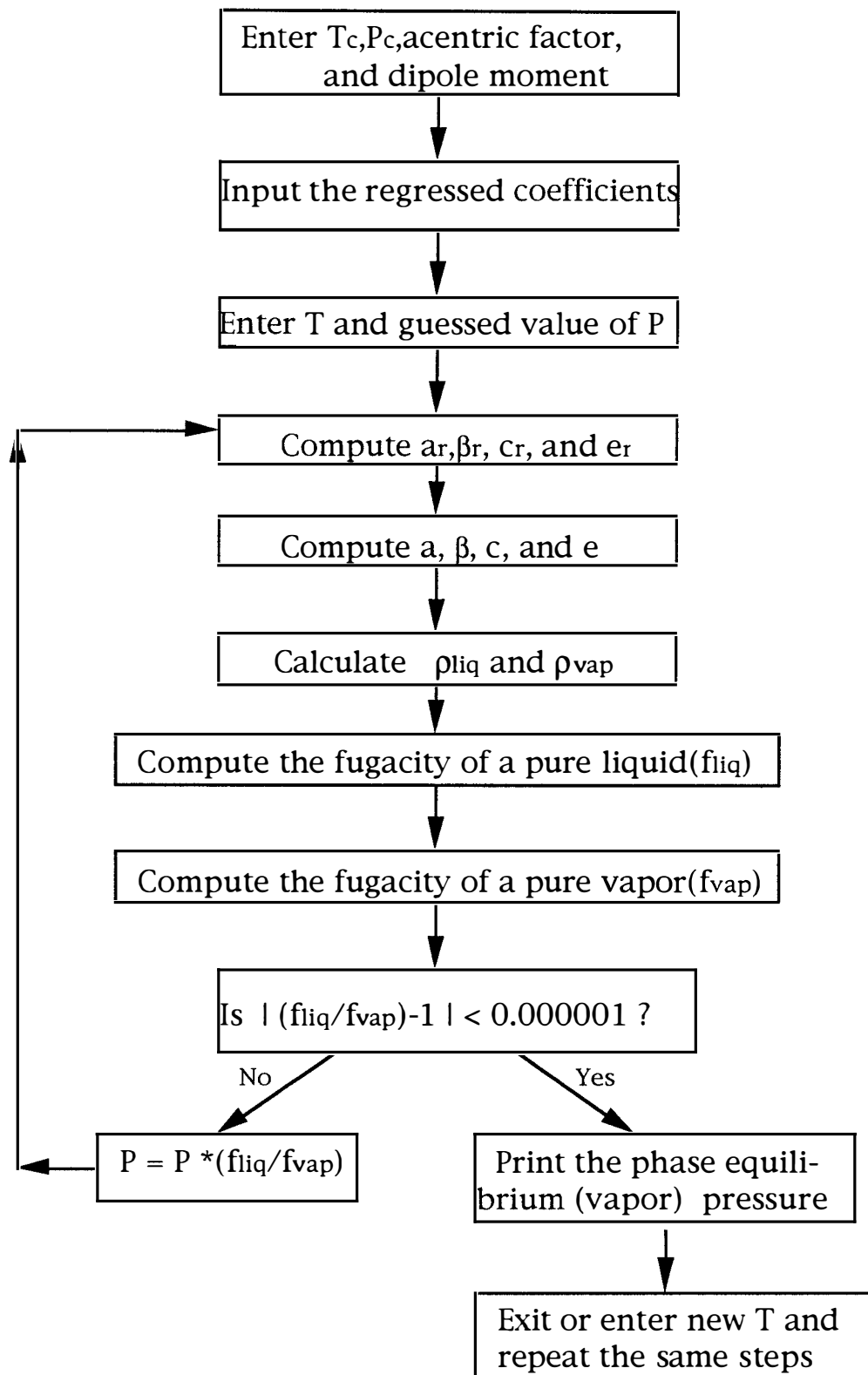


Figure D.1 : Flow chart of a computer program for the calculation of pure fluid phase equilibrium pressure using the generalized quartic equation of state

APPENDIX E

Data Sources

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