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**Watanasiri, Suphat**

**APPLICATION OF MULTIPARAMETER CORRESPONDING STATES  
METHODS TO PREDICT THE THERMODYNAMIC PROPERTIES OF  
NONPOLAR, POLAR, AND ASSOCIATING PURE FLUIDS**

*The University of Oklahoma*

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THE UNIVERSITY OF OKLAHOMA  
GRADUATE COLLEGE

APPLICATION OF MULTIPARAMETER CORRESPONDING STATES METHODS  
TO PREDICT THE THERMODYNAMIC PROPERTIES  
OF NONPOLAR, POLAR, AND ASSOCIATING PURE FLUIDS

A DISSERTATION  
SUBMITTED TO THE GRADUATE FACULTY  
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degree of  
DOCTOR OF PHILOSOPHY

BY  
SUPHAT WATANASIRI  
Norman, Oklahoma

1982

APPLICATION OF MULTIPARAMETER CORRESPONDING STATES METHODS  
TO PREDICT THE THERMODYNAMIC PROPERTIES  
OF NONPOLAR, POLAR, AND ASSOCIATING PURE FLUIDS

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## Abstract

A multiparameter corresponding-states correlation has been developed to accurately predict the thermodynamic properties of nonpolar, polar, and associating pure fluids. The nonpolar contribution to the correlation, developed using multiproperty regression analysis of vapor-pressure, density, and enthalpy-departure data for methane through n-decane, is due to Starling et al. (1978). The polar/associating contribution is developed in this research using multiproperty regression analysis of extensive vapor-pressure, density, and enthalpy-departure data for water, covering all fluid states. The correlation predicts vapor pressure and density for water with percent average absolute relative deviations of 0.6% and 1.4%, respectively. For enthalpy departure, the average absolute deviation is 9.3 kJ/kg (4 Btu/lb).

The correlation is generalized for other polar and associating compounds by using a temperature- and density-dependent factor to characterize their polar/association effects relative to those for water. Parameters in the polar/association factor are determined via multiproperty analysis of vapor-pressure and density data. The

correlation is applied to a wide variety of compounds, including water, ammonia, alcohols, ethers, ketones, mercaptans, amines, phenol, cresols, xylenols, indanols, quinoline, acridine, dibenzofuran, and many other nitrogen-, oxygen-, and sulfur-containing model coal compounds. The average absolute deviations for vapor-pressure, density, and enthalpy and enthalpy-of-vaporization predictions are 1.8%, 2.6%, and 9.5 kJ/kg (4.1 Btu/lb), respectively.

Sensitivity of thermodynamic-property predictions to the values of polar/associative parameters are examined. It is shown that the parameters can be effectively determined using a small number of vapor-pressure and density data. As a result, the correlation can be applied readily to pure compounds with few experimental data. For undefined pseudocomponent fractions, the parameters are determined from the average normal-boiling point, molecular weight, density (at two temperatures), and, if available, the vapor pressure at a temperature lower than the normal-boiling point.

The correlation is used to predict with reasonable accuracy the densities for several wide-boiling coal-fluid fractions from the Exxon-Donor-Solvent process.

APPLICATION OF MULTIPARAMETER CORRESPONDING-STATES METHODS  
TO PREDICT THE THERMODYNAMIC PROPERTIES  
OF NONPOLAR, POLAR, AND ASSOCIATING PURE FLUIDS

CHAPTER I

INTRODUCTION

Several processes have been developed to convert coal into gaseous or liquid fuels. In designing these processes, techniques are needed to estimate the chemical and thermophysical properties of coals and coal fluids. Compared with the essentially paraffinic hydrocarbons from natural gas and petroleum, coal fluids are composed of polycyclic aromatic hydrocarbons with side-chains and with heteroatoms like sulfur, nitrogen, and oxygen. Many compounds identified in coal fluids are highly polar and associative (hydrogen bonded), e.g., phenolic compounds (Schiller, 1977). Consequently, petroleum-based correlations (e.g., Lee and Kesler, 1975; Peng and Robinson, 1976a; Starling et al., 1978) are not applicable to coal fluids. Accurate predictions of thermodynamic properties of model coal compounds and full-range coal fluids would thus

require the use of correlations that are applicable to polycyclic aromatic hydrocarbons and to nonpolar, polar, and associating compounds.

Some progress towards providing thermodynamic correlations for coal fluids has been made in the past few years by the Coal-Calc Project at the University of Oklahoma. A three-parameter corresponding-states modified Benedict-Webb-Rubin (3PCS-MBWR) equation of state (Starling et al., 1978) was modified to predict the thermodynamic properties of nonpolar and slightly polar (reduced dipole moment  $< 0.3$ ) coal chemicals (Brulé et al., 1979, 1982), and their mixtures (Watanasiri et al., 1982) with generally satisfactory results. Results were not as good for highly associative compounds, e.g., cresols, and xylenols, (Brulé et al., 1979, 1982), and for the high-molecular-weight, high-boiling-temperature fractions of coal liquids from the SRC-II and H-coal processes (Watanasiri et al., 1982). The work on the 3PCS-MBWR correlation is reviewed in Chapter II.

Gupta (1981) proposed a five-parameter corresponding-states MBWR correlation for polar and associating one- and two-ring model coal compounds. The correlation predicts vapor pressure and density of these compounds with deviations of 2% and 4%, respectively. However, it fails to give satisfactory prediction accuracy for other polar and hydrogen-bonding compounds such as water, which is an important component in coal liquefaction systems. When the correlation was modified so that



thermodynamic properties for water could be predicted with reasonable levels of accuracy, the density prediction accuracy for model coal compounds suffered. A summary of the work by Gupta is also presented in Chapter II.

The objective of this research is to develop a multiparameter corresponding-states equation of state which is applicable to all classes of fluids, namely, nonpolar, polar, and associating fluids, over all fluid states. Since corresponding states theory does not apply to associating fluids, the present work must be considered empirical. The correlation developed here can be divided into a nonpolar contribution, and a polar/associating contribution. The separation of these different molecular contributions is achieved by the use of a structure factor to characterize structure (size and shape) effects which contribute to the nonpolar part of the correlation. Also, reduced dipole moment is used to characterize the polarity effect, which contributes to the polar/associating part of the correlation. The nonpolar contribution to the new correlation is the 3PCS formulation of Starling et al. (1978) which is briefly reviewed in Chapter II. The polar/associating contribution is based on the correlation of thermodynamic data for water. The water correlation is generalized to other compounds by using a temperature- and density-dependent function to characterize their polar/association effects relative to those for water. Parameters in the polar/association factor are determined

via multiproperty regression analysis of vapor-pressure and density data. The development of the water correlation and the subsequent generalization to other polar/associative fluids are discussed in Chapter III.

This work is primarily aimed at accurate predictions of thermodynamic properties for model coal compounds which are nonpolar, polar, and hydrogen-bonding, and for highly polar and associating compounds, like water, which are of enormous importance in synthetic-fuel processes. The new correlation was successfully applied to water and a wide variety of polar and hydrogen-bonding model coal compounds, including phenol, cresols, xylenols, indanols, furans, thiophenes, quinoline, and acridine. The correlation was further tested on other polar and associating compounds, such as ammonia, straight-chain alcohols, ethers, ketones, mercaptans, and amines. Predictions of vapor pressure, vapor and liquid densities, enthalpy, and enthalpy of vaporization for these compounds are generally satisfactory. Results are presented in Chapter IV.

Chapter V discusses the feasibility of determining the parameters in the polar/associative factor using only a few experimental data points. Also in Chapter V, the correlation is applied to predict the density for several wide-boiling coal-fluid fractions from the Exxon-Donor-Solvent (EDS) process.

## CHAPTER II

### THE THREE- AND FIVE-PARAMETER CORRESPONDING-STATES MBWR CORRELATIONS

This chapter reviews some of the earlier work on applications of corresponding-states methods to predict thermodynamic properties and phase behavior of coal fluids.

#### 2.1 The Three-Parameter Corresponding-States MBWR Correlation

The three-parameter corresponding-states MBWR equation of state (Starling et al., 1978) expresses the compressibility factor  $Z$  as:

$$Z = Z_0(T^*, \rho^*) + \gamma Z_\gamma(T^*, \rho^*) \quad (1)$$

where  $Z_0$  and  $Z_\gamma$  are universal functions of reduced temperature,  $T^*$ , and reduced density  $\rho^*$ . Each compound is characterized by the orientation parameter,  $\gamma$ , which accounts for size, shape, and mild polarity effects of the compound. Equation (1) was developed using vapor-pressure, density and enthalpy-departure data for methane through n-decane with their orientation parameters being forced to

equal Pitzer's acentric factor,  $\omega$ . The orientation parameters for other fluids are determined from regression analysis of thermodynamic data such as vapor pressure, density, and enthalpy data (Brulé et al., 1979). Expressing equation (1) in the form of reduced-temperature and reduced-density expansions, it becomes:

$$\begin{aligned}
 Z = 1 + \rho^* (E_1 - E_2 T^{*-1} - E_3 T^{*-3} + E_9 T^{*-4} - E_{11} T^{*-5}) \\
 + \rho^{*2} (E_5 - E_6 T^{*-1} - E_{10} T^{*-2}) \\
 + \rho^{*5} (E_7 T^{*-1} + E_{12} T^{*-2}) \\
 + E_8 \rho^{*2} T^{*-3} (1 + E_4 \rho^{*2}) \exp(-E_4 \rho^{*2})
 \end{aligned} \tag{2}$$

where

$$T^* = kT/\epsilon \tag{3}$$

$$\rho^* = \rho\sigma^3 \tag{4}$$

and

$$E_i = a_i + \gamma b_i \tag{5}$$

The universal constants  $a_i$  and  $b_i$  were reported by Brulé et al. (1979, 1982), and are listed in Table 2.1. The molecular-energy parameter  $\epsilon$  and molecular-size parameter  $\sigma^3$  are related to critical temperature  $T_c$  and critical density  $\rho_c$ , respectively.

$$\epsilon = kT_c/1.2593 \tag{6}$$

$$\sigma^3 = 0.3189/\rho_c \tag{7}$$

Table 2.1

Universal Constants  $a_i$  and  $b_i$ , to be Used in Equation (5), for the Three-Parameter Corresponding-States MBWR Correlation.

$i$	$a_i$	$b_i$
1	1.45907	0.32872
2	4.98813	-2.64399
3	2.20704	11.3293
4	4.86121	-
5	4.59311	2.79979
6	5.06707	10.3901
7	11.4871	10.3730
8	9.22469	20.5388
9	0.094624	2.76010
10	1.48858	-3.11349
11	0.015273	0.18915
12	3.51486	0.94260

The 3PCS-MBWR equation was originally developed for natural-gas and petroleum-fluid systems. For normal-paraffin hydrocarbons methane through n-decane, the average absolute deviations (averaged over all fluids) are 1.00% for density, 2.63 kJ/kg (1.13 Btu/lb) for enthalpy, and 0.85% for vapor pressure (Starling et al. 1978). The correlation is also accurate in the cryogenic region. In order to apply the 3PCS-MBWR correlation to mixtures, a conformal-solution model was used to express mixture composition dependence. Predictions of mixture thermodynamic properties and phase behavior are generally satisfactory except for mixtures in which the components have large size differences, e.g., methane + n-decane (Starling et al., 1978).

The 3PCS-MBWR correlation was applied to pure coal fluids by determining the orientation parameter,  $\gamma$ , in equation (1), or, equivalently, equation (5), for the fluids. The orientation parameter was obtained by multiproperty regression analysis of vapor-pressure, density, and enthalpy data for the fluids (Brulé et al., 1979, 1982). Using the  $\gamma$  obtained in this manner, the thermodynamic properties of numerous nonpolar, polar, and associating model coal compounds were calculated and compared with experimental values. Results for some representative compounds are presented in Table 2.2. The thermodynamic properties for nonpolar coal chemicals were predicted with acceptable levels of accuracy. For example, for phenanthrene, the deviations in vapor pressure and

Table 2.2

Predictions of Thermodynamic Properties Using Generalized 3PCS-MBWR Correlation.

Compounds	Prop.	N	Range		AARD% <sup>1,2</sup>	Data References
			T, °C	P, kPa		
Furan	Ps	19	0-217	28-5500	3.70	Kudchadker et al. 1978c
Toluene	Ps	42	60-316	19-4068	1.45	Vargaftik, 1975 API-44/TRC
	den.	23	0-110	101	0.91	
	Hd	84	10-371	346-17237	3.03	
o-Cresol	Ps	17	120-417	10-4811	2.04	Jordan, 1954
	den.	22	70-424	0.9-5008	15.9	Kudchadker et al. 1978a
2,4-Xylenol	Ps	15	200-434	76-4400	4.04	Kudchadker et al. 1978b
Thianaphthene	Ps	29	158-357	19-1060	0.55	Wieczorek & Kobayashi 1980
Tetralin	Ps	22	93-446	3-3296	1.10	Kudchadker et al. 1978d
	den.	20	94-400	3-3296	1.89	Kudchadker et al. 1978d
1-Methylnaphthalene	Ps	17	142-246	6-103	1.27	Boublik et al. 1973
Acridine	Ps	9	166-346	1-101	4.82	McNeil 1965
Phenanthrene	Ps	51	199-382	3-200	0.80	Kudchadker et al. 1978e
	den.	8	100-320	1-101	0.67	Kudchadker et al. 1978e

<sup>1</sup> For Ps, and den.,  $AARD\% = \frac{1}{N} \sum |calc-exp|/exp \times 100 \%$ .

<sup>2</sup> For Hd,  $AAD = \frac{1}{N} \sum |calc-exp|$ , in Btu/lb.

density were 0.8% and 0.7%, respectively. The properties for many polar non-associating fluids could also be predicted with reasonable accuracy as long as the compounds are not too polar (reduced dipole moment approximately  $< 0.3$ ). This class of fluids, is exemplified by furan, tetralin, and thianaphthene. For example, for tetralin, the % deviations in vapor pressure and density were 1.1% and 1.9%, respectively. When the fluids were highly polar and also associative, the 3PCS-MBWR correlation could not describe the properties with the same levels of accuracy, e.g., for o-cresol, % deviations for vapor pressure and density were 2.0% and 15.9%, respectively. The less satisfactory results for the polar and associating compounds were attributed to the fact that the 3PCS-MBWR correlation was developed for nonpolar and slightly polar fluids. Highly polar and associative compounds like cresols and xylenols overextend the limits of applicability of the correlation. In fact, there is no theoretical basis for the use of corresponding states methods for associating fluids.

Watanasiri et al. (1982) applied the 3PCS-MBWR correlation using semiempirical exponent conformal-solution mixing rules (Lee et al., 1979), to predict the phase behavior of binary and ternary mixtures of model coal compounds with light gases that are commonly present in coal-conversion process streams. The light components studied were hydrogen, methane, nitrogen, carbon dioxide, carbon monoxide, and hydrogen sulfide. In general, the K-



values of the light components were predicted to within 5% of the experimental values. For the heavy model coal compounds (e.g., tetralin), the % deviations in K-value prediction were usually less than 10%. The exceptions were mixtures involving water and, in some cases, m-cresol. For these mixtures, the K-value deviations were 15% or higher. These results, again, indicate the inadequacy of the 3PCS-MBWR correlation in dealing with highly polar and hydrogen-bonding compounds. Several undefined coal fluids were also studied. Undefined fluids are fluids for which the exact compositions are not known because the compounds making up the fluids are too numerous. Generally, the fluids are broken up into narrow-boiling fractions. Then each fraction is treated as a pseudocomponent in the process calculations. The solubility of hydrogen and also of methane in several narrow-boiling fractions of fluids from the Exxon Donor Solvent (EDS) and Solvent Refined Coal (SRC-II) processes (Lin et al., 1981) were predicted. Most of the prediction results were in error by approximately 10%. However, for the high-molecular-weight, high-boiling-temperature SRC-II fractions, errors were much larger (ca. 30%). The K-values of components in the overhead and bottoms streams from the hot separator following the reactor in the H-Coal pilot plant (IGT, 1980) were also predicted. The K-values of all high-boiling fractions were poorly predicted. The poor results were attributed to the breakdown of the correlations used to predict the characterization parameters for the

fractions (see Brulé et al., 1982). The characterization-parameter correlations were developed using data for coal compounds with maximum boiling points of 300°C. However, many of the fractions in actual process streams have average boiling temperature well in excess of 500°C. Furthermore, the fraction-boiling-temperature range was possibly too wide to satisfy pseudocomponent approximation assumption.

This earlier work in applying the 3PCS-MBWR correlation to pure model coal compounds and defined as well as undefined mixtures of coal fluids, provide impetus for further work on the development of a correlation which is applicable to highly polar and associating compounds as well as nonpolar and slightly polar compounds. The research presented here stems directly from the 3PCS-MBWR work.

Another problem area pointed out in the 3PCS-MBWR work is the inadequacy of characterization-parameter correlations for high-boiling fractions. Brulé and Starling (1982) proposed a method, called Therm-Trans, to overcome this problem. This method utilizes multiproperty analysis of inspection data for the fraction (normal-boiling point, specific gravity, molecular weight, and viscosity) to estimate characterization parameters ( $T_C$ ,  $\rho_C$ ,  $\gamma$ ) for the fraction. This method was tested on numerous coal- and petroleum-fluid fractions with satisfactory results. In this research, the Therm-Trans method is applied in chapter V to coal-fluid fractions. When the new correlation is used to predict the densities and the vapor pressures for several

coal-fluid fractions, some of the characterization parameters are determined using the thermodynamic inspection data.

## 2.2 The Five-Parameter Corresponding-States MBWR Correlation

Gupta (1981) proposed a five-parameter corresponding-states MBWR correlation for polar and associative one- and two-ring coal compounds. The SPCS-MBWR equation is:

$$Z = Z_0(T^*, \rho^*) + \gamma Z_\gamma(T^*, \rho^*) + \mu^{*4} Z_\mu(T^*, \rho^*) + \alpha Z_\alpha(T^*, \rho^*) \quad (8)$$

In equation (8),  $Z_0$  and  $Z_\gamma$  are identical to the corresponding functions in equation (1).

In an attempt to separate the contributions to  $Z$  into structure (size and shape),  $Z_\gamma$ ; polarity,  $Z_\mu$ ; and association,  $Z_\alpha$  contributions, a structure factor,  $\omega_s$ , was used in place of the Pitzer acentric factor,  $\omega$ . Since the acentric factor is defined from reduced vapor-pressure data, it not only contains information about the structure, but also the polarity and the degree of association of the compound. The structure factor is intended to account only for structure effects. A few authors have investigated the separation of the contributions to the acentric factor into shape and polarity effects, e.g., Peng and Stiel (1971). The concept of the structure factor used by Gupta was taken from Eubank and Smith (1962) who used the structure factor

in their thermodynamic correlation for dilute polar gases. In their work, the structure factor for a polar compound was defined as the acentric factor of its homomorph, which is a nonpolar compound that has the same general molecular structure as the polar compound. For polar compounds like those classed as alcohols, ketones, or ethers, the homomorphs have the same general structure as the polar compounds, except that oxygen is replaced by a -CH<sub>3</sub> or a -CH<sub>2</sub>- group. For example, the homomorph for ethanol is propane. Difficulties in choosing the homomorph preclude most inorganic substances from this type of correlation (Eubank and Smith, 1962).

The polar contribution,  $Z_{\mu}$ , is obtained from perturbation theory for dipole-dipole interactions (Twi, 1976). The reduced dipole moment,  $\mu^*$ , is defined as:

$$\mu^* = 100\mu / (1.380535 \sigma^3 \epsilon / k)^{1/2} \quad (9)$$

$$\epsilon / k = T_c / 1.2593 \quad (10)$$

$$\sigma^3 = 0.3189V_c / 0.602252 \quad (11)$$

where  $\mu$  is dipole moment in debye units,  $T_c$  is critical temperature in K,  $V_c$  is critical volume in cc/gmole, and  $\sigma^3$  is molecular volume in  $\text{\AA}^3$ .

The association parameter,  $\alpha$ , was defined as:

$$\alpha = H_v / H_v^i - 1.0 \quad (12)$$

where

$H_v$  = heat of vaporization of

associating fluid at normal boiling point.

$H_v^i$  = heat of vaporization of polar non-associating fluid homolog at normal boiling point.

The association contribution,  $Z_{\alpha}$ , has the same temperature and density dependence as  $Z_0$  and  $Z_{\gamma}$ . The universal constants for  $Z_{\alpha}$  were determined from multiproperty regression analysis of experimental data. When the constants in  $Z_{\alpha}$  were obtained by fitting vapor pressure and density data of one- and two-ring associative aromatic hydrocarbons, the SPCS-MBWR equation predicted vapor pressure and density to 2% and 4%, respectively. However, when the correlation was used to predict vapor pressure and density of other polar and associating fluids such as water and ammonia, the overall deviations for both compounds were  $\sim 10\%$ . Since water is an important component encountered in coal-fluid processing, an attempt was made to improve  $Z_{\alpha}$  such that properties of both aromatic coal compounds and water could be predicted accurately. The constants in  $Z_{\alpha}$  were redetermined by using the data for both coal compounds and water. The predictions of vapor pressures and densities for water were accurate to 1.7% and 1.1%, respectively. For coal fluids, the vapor-pressure prediction error was 5%. However, the density prediction error of 14% was not satisfactory. Equation (8) is probably not applicable to both water and coal chemicals or other associating fluids because  $Z_{\alpha}$  does not adequately represent association

effects. The temperature and density dependence for  $Z_{\alpha}$  could be quite different from  $Z_{\circ}$  and  $Z_{\gamma}$ . Another possibility is that the association parameter,  $\alpha$ , used in equation (8) is not suitable for characterizing the association effects (Gupta, 1981).

Gupta compared the magnitude of all contributions to  $Z$  in equation (8). He reported that the polar contribution,  $\mu^* Z_{\mu}$ , constitutes less than 3% of  $Z$  for compounds with reduced dipole moment smaller than 0.5, but the polar contribution can be appreciable (up to 15%) for compounds with  $\mu^*$  greater than 0.5.

The work of Gupta suggests that additional temperature and density dependence may be required for the associative contribution to  $Z$ . Also the generally small polar contribution may be combined with the associative contribution, without sacrificing prediction accuracy.

### CHAPTER III.

#### A MULTIPARAMETER CORRESPONDING-STATES CORRELATION FOR NONPOLAR, POLAR, AND HYDROGEN-BONDING COMPOUNDS

In this work, an equation of state which is applicable to all classes of fluids, namely, nonpolar, polar, and associating compounds is developed. The correlation can be conveniently divided into nonpolar, and polar/associative contributions. The nonpolar contribution comes from the 3PCS correlation which is an excellent correlation for nonpolar compounds (Starling et al. 1978; Brulé et al., 1979; 1982), as discussed in chapter II. The polar and associative contributions come from the equation of state for water, and are characterized by a reduced dipole moment and an association factor. The development of the new correlation is discussed in this chapter.

The new compressibility factor correlation is expressed as:

$$Z = Z_O(T^*, \rho^*) + \omega_S Z_Y(T^*, \rho^*) + \mu^* F_\alpha(T^*, \rho^*) Z_\alpha(T^*, \rho^*) \quad (13)$$

where  $Z_O$ , and  $Z_Y$  are the same as those in equation (1)

(i.e., the same temperature and density dependence, and numerical constants). The use of  $Z_O$  and  $Z_\gamma$  preserves the capability of the new correlation in predicting accurately the properties of nonpolar compounds ( $\mu^*=0$ ).

As discussed in section 2.2,  $\omega_S$  is the structure factor defined using the homomorph method (Eubank and Smith 1962, Gupta 1981). It is used in the new correlation to account for structure (size and shape) effects in order to separate structural contributions from polarity and association contributions. A homomorph for the compound has to be identified in order to determine  $\omega_S$ . The difficulty and ambiguity in choosing the appropriate homomorph, and hence the structure factor, for a polar or associative compound of interest, as discussed by Eubank and Smith (1962), are partially overcome by the use of a correlation for the structure factor which is a function of critical temperature, critical volume, normal boiling temperature, and dipole moment. The correlation for the structure factor is discussed in section 3.1. Subsequently, this structure factor correlation is used to define  $\omega_S$ .

The reduced dipole moment,  $\mu^*$ , is defined by equations (9) through (11). The parameter  $\mu^*$  is used to characterize polar compounds and to make the polar/association contributions due to  $Z_\alpha$  vanish for the case of nonpolar compounds. For nonpolar compounds ( $\mu^*=0$ ), equation (13) reduces to the 3PCS form of equation (1).

The term  $Z_\alpha$  is the polar and associative contribution



to  $Z$ . The expression for  $Z_\alpha$  is obtained from the equation of state for water. The rationale for the choice of  $Z_\alpha$  and the development of the water equation of state are discussed in sections 3.2 and 3.3. The polar/association factor,  $F_\alpha$ , is used to generalize the correlation to polar and associating fluids. The determination of  $F_\alpha$  is discussed in section 3.4.

### 3.1 Correlation for the Structure Factor

As discussed above, the structure factor is used in the new correlation framework, equation (13), to account for structure (size and shape) effects. The structure factor of a compound is defined as the acentric factor of its homomorph. The homomorph of a polar compound is a nonpolar compound which has the same general structure, normally with the OH, or NH<sub>2</sub> groups being replaced by CH<sub>3</sub> or CH<sub>2</sub> groups. For a nonpolar compound, the homomorph would be, naturally, the compound itself.

The concept of the structure factor, and hence homomorph, is introduced in an attempt to cast the compressibility-factor correlation, equation (13), with a nonpolar contribution that results primarily from structure (size and shape) effects, and with a polar/associative contribution which results from polarity and hydrogen-bonding effects. The fact that the acentric factor,  $\omega$ , represents both structure and polar/associative effects,

precludes  $\omega$  from being used in the new correlation framework. The use of the structure factor, although providing the necessary separation of different molecular contributions, poses several difficulties and ambiguities. One obvious ambiguity is that several polar/associating compounds can have the same homomorph (hence, the same structure factor). For example, the homomorph for methanol, as well as methylamine and methylmercaptan is the nonpolar compound ethane. The structure factors for these three compounds should be different from one another in principle, although the differences could be relatively small, because of the differences in the sizes of oxygen, nitrogen, and sulfur atoms. The homomorph for some polar organic compounds cannot be conveniently defined, i.e., what homomorph should be chosen for toluene ( $\mu^*=0.131$ ), or o-xylene ( $\mu^*=0.152$ ) is not clear. For inorganic compounds, e.g., HCl, the ambiguity of defining a homomorph becomes even more severe.

Despite these drawbacks, the structure factor, defined through the homomorph concept, was shown to be a useful characterization parameter in previous research (Eubank and Smith, 1962; Gupta, 1981), and also in this work, as discussed in the chapter IV. An attempt was made to correlate the structure factors of compounds for which homomorphs can be clearly defined as functions of measurable properties of the compounds (e.g., critical temperature, normal boiling temperature, critical volume, and dipole

moment). The reasons for developing the correlation are twofold. First, given a correlation that can predict the structure factor for any polar and associating compounds of interest with reasonable levels of accuracy, the correlation can then be used as the defining equation for the structure factor. Thus, it is no longer necessary to rely on the homomorph concept to deduce the structure-factor value for a given compound. As a result, the difficulties and ambiguities associated with the use of the homomorph can be totally avoided. Second, the equation of state correlation, equation (13) is ultimately developed to predict the thermodynamic properties for undefined coal-fluids. The structure-factor correlation, which is developed as a function of measurable quantities, would be used in predicting the structure factor for undefined fractions. The correlation for the structure factor is:

$$\begin{aligned}
 f_1 &= 1.60457x \ln(T_c/V_c) \\
 f_2 &= 4.91301 - 8.96259x(T_b/T_c) - 7.51826x(T_b/T_c)^2 \\
 &\quad + 28.5238x(T_b/T_c)^3 + 7.14638x \ln(T_b/T_c) \\
 f_3 &= \mu^* (-96.4516x(T_b/T_c)^{0.5} + 112.424x(T_b/T_c)^{0.2} \\
 &\quad + 5.38401x(T_c/V_c)^{0.5} - 29.3509x(T_c/V_c)^{0.2}) \\
 f_4 &= 100.559 - 40.0325x(T_b/T_c) - 156.114x(T_b/T_c)^2 \\
 &\quad + 104.718x(T_b/T_c)^3 + 72.0599x \ln(T_b/T_c) \\
 \omega_s &= (f_1 + f_2 + f_3)/f_4 \tag{14}
 \end{aligned}$$

where  $T_c$  is the critical temperature in K,  $V_c$  is the

critical volume in cc/gmole,  $T_b$  is the normal boiling temperature in K, and  $\mu^*$  is the reduced dipole moment calculated using equations (9) through (11). The characterization parameters (e.g.,  $T_c$ ) for the compounds used to develop equation (14) are summarized in Table 3.1. The values predicted using equation (14) agree within 16% of the values obtained through the homomorph method, as shown in Table 3.2. The predicted structure factor values for methanol, methylamine, and methylmercaptan are slightly different from one another. The predicted structure factor for toluene is also smaller than its acentric factor. A reasonable value for HCl can also be obtained. These observations indicate that equation (14) is reasonably well behaved and can be used to define the structure factor.

### 3.2 Determination of $Z_\alpha$

Gupta (1981) used for  $Z_\alpha$  a function that has the same temperature and density dependence as  $Z_0$  and  $Z_\gamma$ . However, the temperature and density dependence used by Gupta for  $Z_\alpha$  was not adequate in representing the polar and hydrogen-bonding effects as demonstrated by poor density predictions for these compounds. A  $Z_\alpha$  expression which can adequately represent the pressure-density-temperature behavior of polar and associative compounds is necessarily different from those for  $Z_0$  and  $Z_\gamma$ . In order to develop the expression for  $Z_\alpha$ , extensive and accurate PVT and enthalpy data for polar

**Table 3.1**  
**Characterization Parameters for Polar and Associating Compounds**  
**Used to Develop the  $\omega_s$  Correlation, Equation (14).**

Emp. Form.	Compound Name	MW	Tc K	Tb K	$\rho_c$ kg/m <sup>3</sup>	$\omega_s^*$	$\mu$ debye
H <sub>2</sub> O	Water	18.015	647.3	373.2	321.7	0.008	1.82
NH <sub>3</sub>	Ammonia	17.03	405.6	239.9	234.8	0.008	1.47
CH <sub>4</sub> O	Methanol	32.042	512.6	337.8	271.5	0.098	1.7
C <sub>2</sub> H <sub>6</sub> O	Ethanol	46.069	516.2	351.5	275.9	0.152	1.73
C <sub>3</sub> H <sub>8</sub> O	Propanol	60.096	536.7	370.4	275.0	0.193	1.67
C <sub>4</sub> H <sub>10</sub> O	1-Butanol	74.123	562.9	390.9	270.5	0.251	1.81
C <sub>5</sub> H <sub>12</sub> O	1-Pentanol	88.150	586.0	411.0	270.4	0.296	1.71
C <sub>6</sub> H <sub>14</sub> O	1-Hexanol	102.18	610.0	430.2	268.2	0.351	1.73
C <sub>6</sub> H <sub>6</sub> O	Phenol	94.113	694.2	455.0	411.0	0.257	1.55
C <sub>7</sub> H <sub>8</sub> O	m-Cresol	108.14	705.9	475.4	346.6	0.331	1.59
C <sub>7</sub> H <sub>8</sub> O	o-Cresol	108.14	697.6	464.2	383.5	0.314	1.45
C <sub>7</sub> H <sub>8</sub> O	p-Cresol	108.14	704.6	475.1	390.4	0.324	1.56
C <sub>8</sub> H <sub>10</sub> O	2,4-Xylenol	122.17	707.7	484.1	320.0	0.390	1.98

Table 3.1 (Continued)

Emp. Form.	Compound Name	MW	Tc K	Tb K	$\rho_c$ kg/m <sup>3</sup>	$\omega_s^*$	u debye
C8H10O	2,5-Xylenol	122.17	707.1	484.3	350.0	0.390	1.52
C8H10O	2,6-Xylenol	122.17	701.1	474.2	310.0	0.390	1.90
C8H10O	3,4-Xylenol	122.17	730.0	500.2	350.0	0.390	1.73
C2H6O	Dimethyl Ether	46.069	400.0	248.3	258.8	0.152	1.30
C3H8O	Methyl Ethyl Ether	60.096	437.8	280.5	271.9	0.193	1.22
C4H10O	Diethyl Ether	74.123	466.7	307.7	264.7	0.251	1.30
C5H12O	Ethyl Propyl Ether	88.150	500.6	336.8	258.0	0.296	1.16
C12H10O	Diphenyl Ether	170.21	766.0	531.2	331.0	0.458	1.15
C3H6O	Acetone	58.080	508.2	329.4	278.0	0.176	2.86
C4H8O	2-Butanone	72.107	535.6	352.8	270.1	0.227	2.73
C5H10O	2-Pentanone	86.134	564.0	375.5	286.2	0.279	2.65
CH4S	Methyl Mercaptan	48.107	470.0	279.1	331.8	0.098	1.26
C2H6S	Ethyl Mercaptan	62.134	499.0	308.2	300.2	0.152	1.44
C12H8S	Dibenzothiophene	184.27	899.3	605.3	348.9	0.334	0.83

Table 3.1 (Continued)

Emp. Form.	Compound Name	MW	Tc K	Tb K	$\rho_c$ kg/m <sup>3</sup>	$\omega_s^*$	$\mu$ debye
CH5N	Methylamine	31.058	430.0	266.8	221.8	0.098	1.29
C2H7N	Ethylamine	45.085	456.0	289.7	253.3	0.152	1.35
C2H7N	Dimethylamine	45.085	437.6	280.0	241.1	0.152	1.18
C4H11N	Diethylamine	73.139	496.6	328.6	243.0	0.251	1.12
C6H7N	Aniline	93.129	699.2	457.2	339.9	0.257	1.56
C4H4O	Furan	68.075	490.2	304.5	312.3	0.220	0.70
C4H8O	Tetrahydrofuran	72.107	540.2	339.1	321.9	0.192	1.70
C12H8O	Dibenzofuran	168.20	837.8	557.9	334.0	0.334	0.88
C5H5N	Pyridine	79.102	620.0	388.5	311.4	0.144	2.30
C9H7N	Quinoline	129.161	782.2	510.8	320.7	0.302	2.20
C9H7N	Isoquinoline	129.161	803.2	516.4	320.5	0.282	2.60
C12H9N	Carbazole	167.20	900.1	627.9	267.8	0.401	2.11
C13H9N	Acridine	179.22	905.2	619.2	330.1	0.362	1.96

\*

Structure factor determined using the homomorph method.

Table 3.2

Comparison of the Structure Factors Obtained Using the Homomorph Method and Those Obtained Using a Correlation, Equation (14).

Compound Name	$\omega_S$ Homomorph	$\omega_S$ Correlation
Water	0.008	0.008
Ammonia	0.008	0.007
Methanol #	0.098	0.086
Ethanol	0.152	0.196
Propanol	0.193	0.280
1-Butanol	0.251	0.308
1-Pentanol	0.296	0.357
1-Hexanol	0.351	0.379
Phenol	0.257	0.248
m-Cresol	0.331	0.301
o-Cresol	0.314	0.287
p-Cresol	0.324	0.304
2,4-Xylenol	0.390	0.310
2,5-Xylenol	0.390	0.342
2,6-Xylenol	0.390	0.293
3,4-Xylenol	0.390	0.330
Dimethyl Ether	0.152	0.163
Methyl Ethyl Ether	0.193	0.204
Diethyl Ether	0.251	0.246
Ethyl Propyl Ether	0.296	0.285
Phenyl Ether	0.458	0.378



Table 3.2 (Continued)

Compound Name	$\omega_S$ Homomorph	$\omega_S$ Correlation
Acetone	0.176	0.099
2-Butanone	0.227	0.176
2-Pentanone	0.279	0.209
Methyl Mercaptan <sup>#</sup>	0.098	0.127
Ethyl Mercaptan	0.152	0.160
Dibenzothiophene	0.334	0.327
Methylamine <sup>#</sup>	0.098	0.146
Ethylamine	0.152	0.181
Dimethylamine	0.152	0.201
Diethylamine	0.251	0.258
Aniline	0.257	0.249
Furan <sup>+</sup>	0.220	0.178
Tetrahydrofuran	0.192	0.169
Dibenzofuran <sup>+</sup>	0.334	0.291
Pyridine	0.144	0.155
Quinoline	0.302	0.230
Isoquinoline <sup>+</sup>	0.275	0.202
Carbazole	0.401	0.369
Acridine	0.362	0.332
Diphenylmethane <sup>+</sup>	0.443	0.423

Table 3.2 (Continued)

Compound Name	$\omega_S$ Homomorph	$\omega_S$ Correlation
* Toluene	0.257	0.249
* Hydrogen Chloride	-	0.092

# Homomorph for Methanol, Methylmercaptan, and Methylamine is Ethane.

\* Homomorph for Toluene and HCl cannot be conveniently defined.

+ Values used by Gupta (1981).

and associative compounds are needed in performing multiproperty regression analysis. Since there are very few polar and associating compounds for which extensive and accurate data have been taken, water was chosen as the candidate fluid. Water is highly polar and associative. There are very accurate and extensive PVT and enthalpy data for water, covering wide ranges of temperature and pressure (e.g., Keenan et al., 1969). In addition, water is found in significant amounts at various stages of coal-conversion processes and ancillary refining processes that involve steam-stripping operations. The presence of water in a process stream poses great difficulties in performing process calculations since most commonly used generalized equations of state correlation are not capable of accurately predicting the thermodynamic properties of water. Although numerous activity coefficient models exist that can model water (e.g., Wilson, 1964; Renon and Prausnitz, 1968), the use of equation of state (EOS) correlation in process calculations has several advantages over the use of activity-coefficient models. One major advantage is that in using EOS in phase-equilibrium calculations involving components that are supercritical at the temperature and pressure of interest, the difficulty and ambiguity in defining the reference states for the supercritical components do not arise. For aqueous mixtures, the K-value of the mixture components are generally predicted with unacceptable levels of accuracy using generalized equations

of state (see e.g., Peng et al. 1976b; Watanasiri et. al. 1982), especially when the concentration of water is high. Because of the importance of water, the difficulties in predicting water properties, and the abundance of water thermodynamic data, water is chosen as the fluid on which the  $Z_\alpha$  expression is based. The temperature and density dependence of the  $Z_\alpha$  expression for water will be used for other polar and hydrogen-bonding compounds. Property predictions for other polar and associating compounds ( $\mu^*F_\alpha \neq 0$ ) can be considered as an interpolation between the 3PCS correlation ( $\mu^*F_\alpha = 0$ ) and the water correlation ( $\mu^*F_\alpha = 1$ ).

### 3.3 The Water Equation of State

The equation of state for water is a special case of the general equation for polar and associative fluids, i.e., equation (13). Choosing methane to be the homomorph for water, the  $\omega_S$  used in equation (13) is 0.008. Setting the product  $\mu^*F_\alpha$  to be unity, equation (13) reduces to:

$$Z_{H_2O} = Z_O(T^*, \rho^*) + 0.008 Z_Y(T^*, \rho^*) + Z_\alpha(T^*, \rho^*) \quad (15)$$

The functional forms of  $Z_O$  and  $Z_Y$ , and the constants  $a_i$  and  $b_i$ , were fixed to be the same as those of the 3PCS-MBWR, equation (2). The term  $Z_\alpha$  was then obtained via multiproperty regression analysis of vapor pressure, vapor and liquid density, and enthalpy-departure data for water. The resultant expression for  $Z_\alpha$  is:

$$\begin{aligned}
Z_{\alpha} = & \rho^* (c_1 - c_2 T^{*-1} - c_3 T^{*-3} + c_9 T^{*-4}) \\
& + \rho^{*2} (c_5 - c_6 T^{*-1}) \\
& + \rho^{*5} (c_{15} + c_7 T^{*-1} + c_{12} T^{*-2}) \\
& + c_8 \rho^{*2} T^{*-3} (1 + b_4 \rho^{*2}) \exp(-b_4 \rho^{*2}) \\
& + c_{13} \rho^{*3} T^{*-2} + c_{14} \rho^{*4} T^{*-1} + c_{16} \rho^{*6} T^{*-1} \quad (16)
\end{aligned}$$

The universal constants  $c_1$  through  $c_{16}$  are reported in Table 3.3. As shown in equation (16),  $Z_{\alpha}$  contains all of the density dependence and most of the temperature dependence of  $Z_{\alpha}$ ,  $Z_{\beta}$ , and  $Z_{\gamma}$ , as in equation (2). However,  $Z_{\alpha}$  also requires three additional density-dependent terms ( $\rho^{*3}$ ,  $\rho^{*4}$ , and  $\rho^{*6}$ ) in order to predict the thermodynamic properties of water to reasonable levels of accuracy. The percent average absolute relative deviation in the prediction of vapor-pressure data over the entire saturation curve including the critical point, is 0.6%. The vapor- and liquid-density predictions are accurate to 1.4%. The density data used extended from low temperature liquid (0 °C) to highly compressed high-temperature vapor (1320 °C, 1720 bar). For enthalpy departure, the average absolute deviation is 9.3 kJ/kg (4 Btu/lb). The enthalpy data used cover the temperature range from 10 °C to 1320 °C, and pressure range from 31 bar to 1720 bar. References from which water data were taken are listed in Table 3.4. The prediction results are also reported in Table 3.4. The P-V-T behavior for water predicted by equation (16) is plotted against experimental data in Figure 1.

Table 3.3

Universal Constants  $a_i$ ,  $b_i$  and  $c_i$  to be Used in Equations (16) and (23), for the Multiparameter Corresponding-States Correlation.\*

$i$	$a_i$	$b_i$	$c_i$
1	1.45907	0.32872	0.485914
2	4.98813	-2.64399	-1.06672
3	2.20704	11.3293	5.39716
4	4.86121	-	-
5	4.59311	2.79979	-1.55842
6	5.06707	10.3901	4.70204
7	11.4871	10.3730	3.47628
8	9.22469	20.5388	17.2603
9	0.094624	2.76010	0.497917
10	1.48858	-3.11349	-
11	0.015273	0.18915	-
12	3.51486	0.94260	14.7689
13	-	-	-1.79202
14	-	-	4.78259
15	-	-	7.46297
16	-	-	-23.3345

\*

$a_i$ , and  $b_i$  are the same as those given in Table 2.1, and by Brulé et al. (1982).

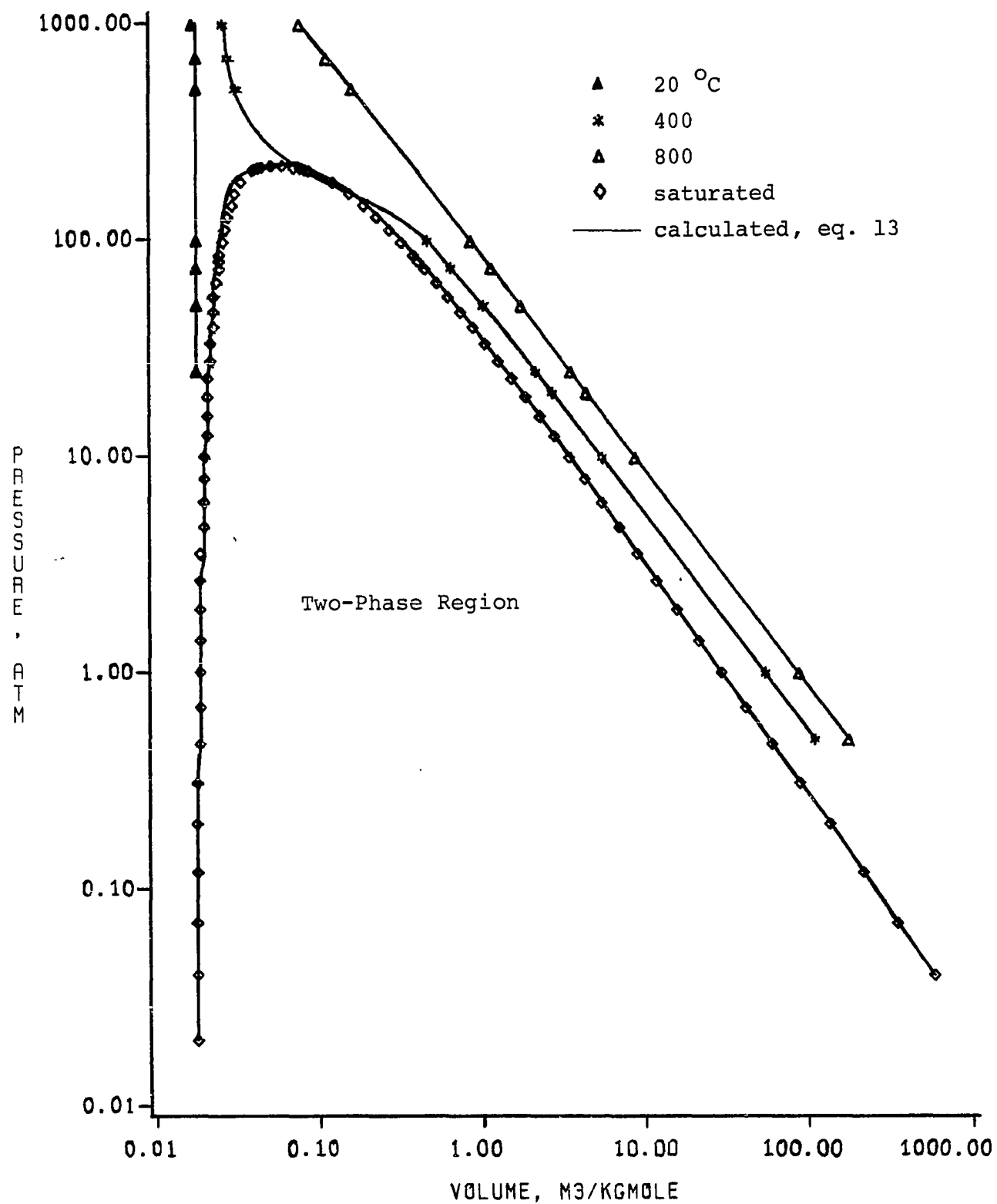
Table 3.4  
Predictions of the Thermodynamic Properties for Water.

Prop. <sup>1</sup>	No. of points	T range K	P range kPa	AARD% <sup>2</sup> eq. (16)	Data References
Ps	65	273-647	0.6-22090	0.62	Osborne et al. 1939.
den.	385	273-1589	0.6-140000	1.46	Osborne et al. 1939, Keyes & Smith 1934, Keyes et al. 1936, Kennedy 1957, Holser & Kennedy 1958, Kell & Walley 1965, Keenan et al. 1969.
Hd	239	283-1589	3100-108400	3.62	Callendar & Egerton 1960, Keenan et al. 1969.

<sup>1</sup> Ps=vapor pressure, den.=density, Hd=enthalpy departure.

<sup>2</sup> AAD for Hd is in Btu/lb.

FIGURE 1.  
EXPERIMENTAL AND PREDICTED WATER DENSITIES





Note that the correlation for water in this work is not as accurate as specific correlations for water, such as the Keenan and Keyes correlation (Keenan et al., 1969). However, it is not the intent of this work to develop a better correlation for water than, e.g., the Keenan and Keyes correlation. The water correlation is used as a vehicle for the extension of the 3PCS-MBWR equation to polar and associative fluids and the levels of accuracy achieved here is adequate for process design. The Keenan and Keyes correlation cannot be used conveniently in our corresponding-states framework because of its complexity.

#### 3.4 Determination of $F_{\alpha}$

The polar/association contribution to  $Z$ ,  $Z_{\alpha}$ , obtained for water, as explained in the preceding section, is incorporated into the three-parameter corresponding-states correlation, resulting in an equation of state for nonpolar compounds and water.

$$Z = Z_0(T^*, \rho^*) + \omega_S Z_{\gamma}(T^*, \rho^*) + Z_{\alpha}(T^*, \rho^*) \quad (17)$$

The generalization of equation (17) to other polar and hydrogen-bonding compounds must be accomplished by using characterization parameters which force the polar/associative contributions to go to zero for nonpolar compounds, and indicate the degree of polarity and association for the compound. One possible characterization

parameter is the dipole moment (or the reduced dipole moment). However, the dipole moment is not an entirely adequate characterization parameter for compounds that associate or hydrogen-bond. Nonetheless, if one postulates that there exists a function that can characterize the polar and association effects, then equation (17) becomes

$$Z = Z_O(T^*, \rho^*) + \omega_S Z_Y(T^*, \rho^*) + \mu^* F_\alpha Z_\alpha(T^*, \rho^*) \quad (18)$$

The first requirement is met by equation (18). To determine  $F_\alpha$ , equation (18) can be rearranged:

$$F_\alpha = (Z - Z_O(T^*, \rho^*) - \omega_S Z_Y(T^*, \rho^*)) / \mu^* Z_\alpha(T^*, \rho^*) \quad (19)$$

Using isothermal and isochoric data for methanol and ethanol, the functionality of  $F_\alpha$  was determined to be:

$$F_\alpha = d_1 + d_2 \rho^{*2} + d_3 T^* \quad (20)$$

where  $d_1$ ,  $d_2$ , and  $d_3$  are the polar/associative characterization parameters.

### 3.5 The New Equation of State for Nonpolar, Polar, and Associating Compounds

Assembling all the building blocks as described above, the multiparameter corresponding-states correlation for nonpolar, polar, and associating pure fluids is:

$$Z = Z_O(T^*, \rho^*) + \omega_S Z_Y(T^*, \rho^*) + \mu^* F_\alpha(T^*, \rho^*) Z_\alpha(T^*, \rho^*) \quad (21)$$

Expressed as an explicit reduced density and reduced

temperature function, equation (21) becomes:

$$\begin{aligned}
 Z = & 1 + \rho^* (E_1 - E_2 T^{*-1} - E_3 T^{*-3} + E_9 T^{*-4} - E_{11} T^{*-5}) \\
 & + \rho^{*2} (E_5 - E_6 T^{*-1} - E_{10} T^{*-2}) \\
 & + \rho^{*5} (E_{15} + E_7 T^{*-1} + E_{12} T^{*-2}) \\
 & + E_8 \rho^{*2} T^{*-3} (1 + E_4 \rho^{*2}) \exp(-E_4 \rho^{*2}) \\
 & + E_{13} \rho^{*3} T^{*-2} + E_{14} \rho^{*4} T^{*-1} + E_{16} \rho^{*6} T^{*-1} \quad (22)
 \end{aligned}$$

where

$$E_i = a_i + \omega_s b_i + \mu^* F_\alpha c_i \quad (23)$$

and 
$$F_\alpha = d_1 + d_2 \rho^{*2} + d_3 T^* \quad (24)$$

The values of the universal constants  $a_i$ ,  $b_i$ , and  $c_i$  are listed in Table 3.3. The constants  $a_i$  and  $b_i$  (constants for  $Z_o$  and  $Z_\gamma$ , respectively) are the same as those for the 3PCS-MBWR correlation (see Table 2.1), while the  $c_i$  (constants for  $Z_\alpha$ ) are determined from fitting water data, as discussed in section 3.3. The reduced dipole moment,  $u^*$ , is defined in equations (9), through (11). The polar/association parameters,  $d_1$ ,  $d_2$ , and  $d_3$  are determined from experimental vapor pressure and density data, as discussed in Chapter IV.

## CHAPTER IV

### APPLICATION OF THE CORRELATION TO POLAR AND ASSOCIATING PURE COMPOUNDS

#### 4.1 Thermodynamic Property Expressions and Calculations

To calculate thermodynamic properties of a compound (e.g., density, enthalpy, entropy, etc...) at a given temperature and pressure (and composition in the case of mixture), one starts with the determination of density. Density is calculated implicitly by solving equation (22). The density-search technique used in this work was described by Goin (1978). Other thermodynamic properties can then be calculated using the obtained density in the expressions derived by the classical thermodynamic relations (see, e.g., Reid et al. 1977). An example is the following relation for the enthalpy departure:

$$H - H^0 = -\frac{\epsilon}{k}RT^2 \int_0^{\rho^*} (\partial Z / \partial T^*)_{\rho^*} d \ln \rho^* + RT(Z - 1) \quad (25)$$

The expression for enthalpy departure and fugacity are given

in the appendix A.

To calculate the vapor pressure for a compound, one calculates the fugacity of the compound in both the vapor and liquid phases at an assumed initial pressure. Since the fugacities in both phases are equal at the vapor pressure, the initial pressure can be adjusted until the equality of vapor- and liquid-phase fugacities is obtained. The final pressure is the desired vapor pressure. To calculate the enthalpy of vaporization, one calculates the difference between the vapor and liquid enthalpy departure.

#### 4.2 Compound Data Base

The multiparameter corresponding-states correlation is applied to a wide variety of compounds including water, ammonia, alcohols, ethers, ketones, amines, mercaptans, phenol, cresols, xylenols, indanols, quinoline, furans, and many nitrogen-, oxygen-, and sulfur-containing compounds. Some very important model coal compounds like phenanthrol are not included because of the lack of experimental data. Table 4.1 lists the compounds and their characterization parameters.

The characterization parameters  $T_c$  and  $\rho_c$  are taken from the compilation of Reid et al. (1977), or from the literature sources from which thermodynamic data were obtained (e.g., Kudchadker et al., 1977, for phenol). The structure factor,  $\omega_S$ , is obtained using the homomorph method

Table 4.1

Characterization Parameters for Polar and Associating Compounds Studied in This Work<sup>1,2</sup>

Compound Name	$T_C$ K	$V_C$ cc/gmole	$\omega_S$	$\mu^*$	$d_1\mu^*$	$d_2\mu^*$	$d_3\mu^*$
Water	647.3	56.0	0.008	1.255	1.0059	0.0139	-0.0140
Ammonia	405.6	72.5	0.008	1.125	0.8610	-0.0882	-0.0953
Methanol	512.6	118.0	0.098	0.907	1.8716	-0.5746	-0.6273
Ethanol	516.2	167.0	0.152	0.773	2.4803	-0.6236	-1.3846
Propanol	536.7	218.5	0.193	0.640	2.2780	-0.2756	-1.3725
1-Butanol	562.9	274.0	0.251	0.605	0.7994	0.2183	0.0147
1-Pentanol	586.0	326.0	0.296	0.514	2.2580	-0.7885	-1.6159
1-Hexanol	610.0	381.0	0.351	0.471	3.2747	-5.1905	-2.6191
Phenol	694.2	229.0	0.257	0.510	1.9494	-3.8521	-1.3237
m-Cresol	705.9	312.0	0.331	0.445	1.3389	-1.3922	-0.9019
o-Cresol	697.6	282.0	0.314	0.429	1.2935	-3.0866	-0.6992
p-Cresol	704.6	277.0	0.324	0.463	1.5877	-4.3603	-0.7596
2,3-Xylenol	723.0	359.3	0.390	0.510	1.4003	-3.3180	-1.1300
2,4-Xylenol	707.7	381.8	0.390	0.500	0.8796	-0.5009	-0.7658

Table 4.1 (Continued)

Compound Name	T <sub>c</sub> K	V <sub>c</sub> cc/gmole	$\omega_s$	$\mu^*$	$d_1\mu^*$	$d_2\mu^*$	$d_3\mu^*$
2,5-Xylenol	707.1	349.0	0.390	0.402	1.4065	-2.1971	-1.0421
2,6-Xylenol	701.1	394.1	0.390	0.474	0.9385	-3.2931	-0.7711
3,4-Xylenol	730.0	349.1	0.390	0.450	1.6339	-2.0874	-1.2496
2-Indanol	645.7	410.5	0.303	0.472	4.8754	-2.5390	-2.0303
4-Indanol	755.7	395.5	0.303	0.420	0.5154	0.2332	-0.0789
5-Indanol	765.8	395.5	0.303	0.417	0.1190	0.3725	0.3824
Dimethyl Ether	400.0	178.0	0.152	0.639	0.3013	0.4167	-0.2783
Methyl Ethyl Ether	437.8	221.0	0.193	0.515	0.4779	-0.2217	-0.3556
Diethyl Ether	466.7	280.0	0.251	0.472	0.5975	-0.8432	-0.4280
Ethyl Propyl Ether	500.6	341.7	0.296	0.368	-0.3267	0.4550	0.2453
Phenyl Ether	766.0	514.3	0.458	0.240	-0.4015	.00019	0.4187
Acetone	508.2	209.0	0.176	1.152	0.4730	-0.1184	.03743
2-Butanone	535.6	267.0	0.227	0.948	-.00028	0.4976	0.2490
2-Pentanone	564.0	301.0	0.279	0.844	0.4899	-0.9539	-0.1660

Table 4.1 (Continued)

Compound Name	T <sub>C</sub> K	V <sub>C</sub> cc/gmole	ω <sub>S</sub>	μ <sup>*</sup>	d <sub>1</sub> μ <sup>*</sup>	d <sub>2</sub> μ <sup>*</sup>	d <sub>3</sub> μ <sup>*</sup>
Methyl Mercaptan	470.0	145.0	0.098	0.633	0.2241	-0.2133	-0.01414
Ethyl Mercaptan	499.0	207.0	0.152	0.588	0.2240	0.2989	-0.1876
Thiophene	579.4	218.5	0.192	0.188	0.3094	-0.5596	-0.2149
Tetrahydrothiophene	632.0	262.0	0.192	0.613	.01012	0.4739	-.03352
Thianaphthene	752.0	385.0	0.288	0.151	0.2855	-1.9178	-0.1012
Dibenzothiophene	899.3	528.2	0.334	0.158	0.8689	-2.1454	-0.5773
Methylamine	430.0	140.0	0.098	0.690	1.1565	.05413	-0.8730
Ethylamine	456.0	178.0	0.152	0.622	0.7017	-.01382	-0.3671
Dimethylamine	437.6	187.0	0.152	0.541	1.1378	-0.5618	-0.7980
Diethylamine	496.6	301.0	0.251	0.380	0.3088	0.3501	-0.2780
Aniline	699.2	274.0	0.257	0.471	0.8072	-0.5633	-0.4364
Furan	490.2	218.0	0.2201	0.281	-.02964	0.5541	-.07590
Tetrahydrofuran	540.2	224.0	0.1923	0.642	0.2711	-0.4811	-.07554
Dibenzofuran	837.8	503.6	0.334	0.178	-0.6653	0.6710	0.5614



Table 4.1 (Continued)

Compound Name	$T_C$ K	$V_C$ cc/gmole	$\omega_s$	$\mu^*$	$d_1 \mu^*$	$d_2 \mu^*$	$d_3 \mu^*$
Pyridine	620.0	251.0	0.1437	0.761	0.6094	.03640	-0.4710
Quinoline	782.2	402.8	0.302	0.514	0.4402	-0.5312	-0.3564
Isoquinoline	803.2	403.0	0.282	0.600	0.4169	-0.7927	-0.3495
Carbazole	900.1	624.3	0.401	0.369	0.1928	0.6526	-0.2617
Acridine	905.2	542.9	0.362	0.367	-.4765	0.6052	0.6468
Toluene	591.7	316.0	0.257	0.131	-.0187	0.1493	.02001
o-Xylene	630.2	369.0	0.314	0.152	-0.1942	-0.3597	0.1458
Diphenylmethane	770.2	529.1	0.4427	0.072	0.3191	-1.0624	-0.1427
Acetic Acid	594.4	171.0	0.176	0.535	0.8872	-0.5330	0.1573

1  $\omega_s$  determined using the homomorph method.

2  $d_1$ ,  $d_2$ , and  $d_3$  determined by multiproperty analysis of all available vapor pressure and density data.

and the correlation, equation (14), as discussed in section 3.1. Using two different methods to obtain  $\omega_S$ , resulted in slightly different property prediction accuracies, as discussed in the next section. The  $\omega_S$  values reported in Table 4.1 are obtained using the homomorph method. The dipole moment,  $\mu$ , to be used in calculating  $\mu^*$  via equations (9) through (11), is obtained from McClellan (1963). There are many sets of dipole moment values for some compounds, depending on temperature, phase (gas or liquid), and the fluid medium in which the measurement was made (e.g., in benzene, carbon tetrachloride). The recommended values given by McClellan (1963) are generally adopted. If a recommended value is not given, the value for the compound in its liquid state measured in benzene at a temperature of 20-50 °C is used throughout this work, for consistency. The polar/associative characterization parameters  $d_1$ ,  $d_2$ , and  $d_3$  used in equation (24), are not measurable properties, unlike  $T_C$  or  $\rho_C$ , and must therefore be determined by regression analysis of experimental vapor pressure and/or density data. These polar/associative parameters are also dependent on the choice of  $\omega_S$  values being used. The  $d_1$ ,  $d_2$ , and  $d_3$  reported in Table 4.1 are those obtained using vapor pressure and density data, with  $\omega_S$  values determined by the homomorph method. Chapter V discusses the determination of  $d_1$ ,  $d_2$ , and  $d_3$  using different types of thermodynamic property data, and using data sets of different sizes. The effects of these parameters on the accuracy of thermodynamic property

predictions over the complete data set are also discussed. In this chapter,  $d_1$ ,  $d_2$ , and  $d_3$  are determined from the complete set of vapor pressure and density data. The regression method developed by Goin (1978) is used in the determination of parameters throughout this work with the exception of certain parts of chapter V wherein the regression method of Britt-Luecke (1973) is used. In chapter V, three parameters have to be determined using three data points; the regression method of Goin is not applicable in this case.

The experimental thermodynamic data used in this work to determine polar/associative parameters and to test the applicability of the new correlation are vapor pressure, vapor and liquid density, compressibility factor, enthalpy departure, and enthalpy of vaporization. The compound names, temperature and pressure ranges for the experimental data, and references from which the data were taken are listed in Table 4.2. Most of the data are at saturation conditions except for water, ammonia, methanol, ethanol, and dibenzofuran.

#### 4.3 Application of the New Correlation to Polar and Associating Compounds

The polar/associative parameters,  $d_1$ ,  $d_2$  and  $d_3$  determined from vapor pressure and density data with  $\omega_s$  determined from the homomorph method, are used in the first set of calculations. These characterization parameters are

Table 4.2

Temperature and Pressure Ranges, and Data References for the Polar and Associating Compounds Studied in This Work.

Compound	Prop.	No. of points	T range K	P range kPa	Data References
Water	Ps	65	273-647	0.6-22090	Osborne et al. 1939 Osborne et al. 1939, Keyes & Smith 1934, Keyes et al. 1936, Kennedy 1957, Holser & Kennedy 1958, Kell & Walley 1965, Keenan et al. 1969 Callendar & Egerton 1960, Keenan et al. 1969
	den.	385	273-1589	0.6-140000	
	Hd	239	283-1589	3100-108400	
Ammonia	Ps	142	197-403	7-10903	Garnjost 1974, Haar & Gallagher 1977 Garnjost 1974, Haar & Gallagher 1977
	den.	239	197-573	7-81060	
Alcohols					
Methanol	Ps	25	263-503	2-6700	Young 1910 Young 1910, Ramsey & Young 1887
	den.	209	273-513	4-7400	
Ethanol	Ps	38	293-498	6-4700	Young 1910 Ramsey & Young 1887, Young 1910 Lo & Stiel 1969
	den.	214	273-623	2-68900	
	Z	162	473-623	8300-68900	

Table 4.2 (continued)

Compound	Prop.	No. of points	T range K	P range kPa	Data References
Propanol	Ps	44	303-513	4-3550	Kenne & Kreps 1969, Ambrose & Townsend 1963, Ambrose & Sprake 1970 Int. Crit. Tables 1926
	den.	37	353-533	50-4810	
1-Butanol	Ps	41	333-399	8-130	Kenne & Kreps 1969, Ambrose & Townsend 1963, Ambrose & Sprake 1970 Hales & Ellender 1976
	den.	14	293-490	0.6-1300	
1-Pentanol	Ps	44	343-429	6-180	Kenne & Kreps 1969, Ambrose & Sprake 1970 Hales & Ellender 1976
	den.	14	293-490	0.2-800	
1-Hexanol	Ps	42	313-438	0.3-130	Kenne & Kreps 1969
Phenols					
Phenol	Ps	14	323-673	0.3-5100	Kudchadker et al. 1977 Kudchadker et al. 1977 Kudchadker et al. 1977
	den.	14	323-673	0.3-5100	
	H	14	323-673	0.3-5100	
m-Cresol	Ps	23	323-693	0.01-3830	Kudchadker et al. 1978a Kudchadker et al. 1978a Kudchadker et al. 1978a
	den.	26	293-693	0.1-3830	
	H	23	323-693	0.01-3830	
o-Cresol	Ps	23	323-693	0.3-4810	Kudchadker et al. 1978a Kudchadker et al. 1978a Kudchadker et al. 1978a
	den.	24	313-693	0.1-4810	
	H	23	323-693	0.3-4810	

Table 4.2 (continued)

Compound	Prop.	No. of points	T range K	P range kPa	Data References
p-Cresol	Ps	22	333-693	0.2-4280	Kudchadker et al. 1978a
	den.	24	313-693	0.05-4280	Kudchadker et al. 1978a
	H	22	333-693	0.2-4280	Kudchadker et al. 1978a
2,3-Xylenol	Ps	19	353-693	0.5-3400	Kudchadker et al. 1978b
	H	19	353-693	0.5-3400	Kudchadker et al. 1978b
2,4-Xylenol	Ps	32	303-673	0.02-2900	Kudchadker et al. 1978b
	den.	5	303-343	0.02-0.4	Kudchadker et al. 1978b
	H	19	343-673	0.4-2900	Kudchadker et al. 1978b
2,5-Xylenol	Ps	18	353-673	0.7-3200	Kudchadker et al. 1978b
	den.	7	353-473	0.7-76	Kudchadker et al. 1978b
	H	18	353-673	0.7-3200	Kudchadker et al. 1978b
2,6-Xylenol	Ps	17	333-653	0.4-2400	Kudchadker et al. 1978b
	H	18	333-653	0.4-2400	Kudchadker et al. 1978b
3,4-Xylenol	Ps	19	353-693	0.3-3200	Kudchadker et al. 1978b
	den.	7	353-473	0.3-49	Kudchadker et al. 1978b
	H	19	353-693	0.3-3200	Kudchadker et al. 1978b
Indanols					
1-Indanol	Ps	6	333-413	0.02-3	Viswanath & Wilhoit 1980
	den.	6	333-413	0.02-3	Viswanath & Wilhoit 1980
	H	6	333-413	0.02-3	Viswanath & Wilhoit 1980

Table 4.2 (continued)

Compound	Prop.	No. of points	T range K	P range kPa	Data References
2-Indanol	Ps	10	353-513	0.03-115	Viswanath & Wilhoit 1980
	den.	10	353-513	0.03-115	Viswanath & Wilhoit 1980
	H	10	353-513	0.03-115	Viswanath & Wilhoit 1980
4-Indanol	Ps	12	353-553	0.2-235	Viswanath & Wilhoit 1980
	den.	12	353-553	0.2-235	Viswanath & Wilhoit 1980
	H	12	353-553	0.2-235	Viswanath & Wilhoit 1980
5-Indanol	Ps	11	353-533	0.2-139	Viswanath & Wilhoit 1980
	den.	12	353-553	0.2-326	Viswanath & Wilhoit 1980
	H	11	353-533	0.2-139	Viswanath & Wilhoit 1980
<b>Ethers</b>					
Dimethyl Ether	Ps	17	249-393	100-4700	Int. Crit. Tables 1926
	den1	19	249-400	100-5300	Int. Crit. Tables 1926
	denv	19	249-400	100-5300	Int. Crit. Tables 1926
Methyl Ethyl Ether	Ps	18	281-438	100-4400	Int. Crit. Tables 1926
	den1	17	281-438	100-4400	Int. Crit. Tables 1926
	denv	18	281-438	100-4400	Int. Crit. Tables 1926
Diethyl Ether	Ps	24	263-466	150-3600	Int. Crit. Tables 1926
	den1	23	273-467	250-3600	Int. Crit. Tables 1926
	denv	23	273-466	250-3600	Int. Crit. Tables 1926
Ethyl Propyl Ether	Ps	17	334-493	100-2900	Int. Crit. Tables 1926
	den1	18	334-501	100-3300	Int. Crit. Tables 1926

Table 4.2 (continued)

Compound	Prop.	No. of points	T range K	P range kPa	Data References
Diphenyl Ether	Ps	13	523-643	80-700	Vargaftik 1975
	denl	23	523-633	80-600	Vargaftik 1975
Ketones					
Acetone	Ps	20	329-508	100-4800	Int. Crit. Tables 1926
	denl	20	329-508	100-4800	Int. Crit. Tables 1926
	denv	19	329-508	100-4800	Int. Crit. Tables 1926
2-Butanone	Ps	17	316-362	30-130	Collerson et al. 1965
	denl	4	273-303	100	Timmermans 1950
2-Pentanone	Ps	18	330-385	20-130	Collerson et al. 1965
	denl	18	330-385	20-130	Meyer & Wagner 1966
Furans					
Furan	Ps	25	193-473	0.08-4390	Kudchadker et al. 1978c
	denl	20	193-373	0.08-730	Kudchadker et al. 1978c
	H	25	193-473	0.08-4390	Kudchadker et al. 1978c
Tetrahydrofuran	Ps	25	253-540	2-5200	Kudchadker et al. 1978c
	denl	10	253-333	2-80	Kudchadker et al. 1978c
	H	24	253-533	2-4720	Kudchadker et al. 1978c
Dibenzofuran	Ps	19	435-618	5-300	Sivaraman & Kobayashi 1981
	denl	42	391-563	500-25500	Nasir et al. 1981



Table 4.2 (continued)

Compound	Prop.	No. of points	T range K	P range kPa	Data References
<b>Sulfur-Containing Compounds</b>					
Methyl Mercaptan	Ps	21	279-470	100-7200	Int. Crit. Tables 1926
	denl	21	279-470	100-7200	Int. Crit. Tables 1926
Ethyl Mercaptan	Ps	21	308-499	100-5500	Int. Crit. Tables 1926
	denl	21	308-499	100-5500	Int. Crit. Tables 1926
	denv	21	308-499	100-5500	Int. Crit. Tables 1926
Thiophene	Ps	29	235-579	0.2-5700	Kudchadker et al. 1981b
	denl	15	273-393	3-300	Kudchadker et al. 1981b
	H	28	235-573	0.2-5300	Kudchadker et al. 1981b
Tetrahydrothiophene	Ps	33	208-613	0.001-4100	Kudchadker et al. 1981b
	denl	9	273-343	0.5-20	Kudchadker et al. 1981b
	H	24	213-453	0.002-410	Kudchadker et al. 1981b
Thianaphthene	Ps	27	424-631	20-1100	Wieczorek & Kobayashi 1980
Dibenzothiophene	Ps	19	425-608	0.5-100	Sivaraman & Kobayashi 1981
<b>Amines</b>					
Methylamine	Ps	17	267-430	100-7500	Int. Crit. Tables 1926
Ethylamine	Ps	18	290-456	100-5600	Int. Crit. Tables 1926
Dimethylamine	Ps	18	280-438	100-5200	Int. Crit. Tables 1926

Table 4.2 (continued)

Compound	Prop.	No. of points	T range K	P range kPa	Data References
Diethylamine	Ps	19	328-497	100-3700	Int. Crit. Tables 1926
	denl	19	328-497	100-3700	Int. Crit. Tables 1926
	denv	19	328-497	100-3700	Int. Crit. Tables 1926
Aniline	Ps	30	273-699	0.01-5310	Kudchadker 1982
	denl	31	273-699	0.01-5310	Kudchadker 1982
	H	29	273-673	0.01-4040	Kudchadker 1982
Nitrogen-Containing Compounds					
Pyridine	Ps	46	253-620	0.1-5600	Kudchadker 1979
	denl	27	253-620	0.1-5600	Kudchadker 1979
	H	26	253-613	0.1-5210	Kudchadker 1979
Quinoline	Ps	42	313-753	0.03-3500	Viswanath 1979a, Wilson et al. 1981
	denl	16	303-513	0.01-100	Viswanath 1979a
	H	23	303-653	0.01-1148	Viswanath 1979a,
Isoquinoline	Ps	29	333-803	0.1-5000	Viswanath & Wilhoit 1979b
	denl	19	333-533	0.1-150	Viswanath & Wilhoit 1979b
	H	20	333-573	0.1-310	Viswanath & Wilhoit 1979b
Carbazole	Ps	26	518-673	7-220	McNeil 1965, Kudchadker et al. 1981a
	denl	6	520-593	7-50	McNeil 1965, Kudchadker et al. 1981a
	H	10	519-673	7-220	Kudchadker et al. 1981a

Table 4.2 (continued)

Compound	Prop.	No. of points	T range K	P range kPa	Data References
Acridine	Ps	25	383-633	0.05-130	McNeil 1965,
	denl	12	393-613	0.08-90	Kudchadker et al. 1981a
	H	15	383-633	0.05-130	Kudchadker et al. 1981a
Other Compounds					
Toluene	Ps	33	273-583	0.9-3800	Vargaftik 1975
	denl	13	273-383	0.9-100	Vargaftik 1975
o-Xylene	Ps	42	253-632	0.03-3800	Vargaftik 1975
	denl	59	298-548	100-40000	Vargaftik 1975
Diphenylmethane	Ps	38	425-728	4-1800	Wieczorek & Kobayashi 1980
	denl	3	311-372	100	Wilson et al. 1981 API-42, 1966
Acetic Acid	Ps	22	392-595	100-5800	Int. Crit. Tables 1926
	denl	22	392-595	100-5800	Int. Crit. Tables 1926

†

Ps = vapor pressure, den. = vapor and liquid density, denl = liquid density, densv = vapor density, Hd = enthalpy departure, H = enthalpy of vaporization, Z = compressibility factor.

summarized in Table 4.1. Calculations of density, vapor pressure, and enthalpy departure for compounds listed in Table 4.2 were made using equations (22) through (24) and thermodynamic relations in appendix A. The prediction results are presented in Table 4.3. Satisfactory prediction accuracy was achieved using the new equation of state for all of the compounds studied, especially for model coal compounds (e.g., phenol, cresols, xylenols, indanols, pyridine, quinoline, furans), and straight-chain alcohols. The AARD% for vapor pressure and density predictions are 2.3% and 2.8%, respectively.

To provide further perspective on the accuracy achieved by the new correlation, property calculations were made using the 3PCS-MBWR, equation (2). In these calculations, the best orientation parameter determined by regression analysis of all available experimental data are used. The 3PCS-MBWR results, as reported in Table 4.3, reemphasize the inadequacy of three-parameter corresponding-states correlations in predicting properties for highly polar and hydrogen-bonding compounds.

As discussed in section 3.1, the structure factor,  $\omega_S$ , can be conveniently determined using equation (14). In this section, the value of the  $\omega_S$  correlation, and the effects of the  $\omega_S$  values obtained in this manner on the predictions of thermodynamic properties are examined. The  $\omega_S$  values calculated from equation (14) are used in the multiproperty regression analysis of vapor pressure and

**Table 4.3**  
**Predictions of the Thermodynamic Properties for Polar**  
**and Associative Compounds.**

Compound	Prop.	No. of points	AARD%		3PCS-MBWR
			eq. 13	eqs. 13&14	
Water	Ps	64	0.57	0.57	11.9
	den.	385	1.46	1.46	6.47
	Hd	239	3.62	3.63	18.1
Ammonia	Ps	142	0.44	0.44	4.10
	den.	239	0.88	0.88	4.30
-----    Alcohols    -----					
Methanol	Ps	25	4.27	4.38	9.70
	den.	209	2.50	2.52	4.30
Ethanol	Ps	38	3.44	3.22	2.60
	den.	214	3.79	3.85	4.40
	z	162	1.73	1.57	3.70
Propanol	Ps	44	2.29	2.33	6.30
	den.	37	3.64	3.79	5.10
1-Butanol	Ps	41	7.0	0.33	4.60
	den.	14	5.90	0.89	0.50
1-Pentanol	Ps	44	1.65	1.65	4.80
	den.	14	0.76	0.79	0.90
1-Hexanol	Ps	42	1.17	1.13	8.10
-----    Phenols    -----					
Phenol	Ps	14	3.22	1.83	2.40
	denl	14	2.99	4.03	19.7
m-Cresol	Ps	23	2.89	2.93	3.20
	denl	26	1.30	1.23	7.50
o-Cresol	Ps	23	2.30	2.12	2.30
	denl	24	2.90	2.85	15.7

Table 4.3 (continued)

Compound	Prop.	No. of points	eq. 13	AARD±	
				eqs. 13&14	3PCS-MBWR
p-Cresol	Ps	22	3.68	3.52	4.20
	denl	24	3.02	2.97	20.1
2,3-Xylenol	Ps	19	3.48	3.61	4.96
2,4-Xylenol	Ps	32	3.72	3.77	8.42
	denl	5	1.33	1.25	0.19
2,5-Xylenol	Ps	18	4.53	4.63	5.13
	denl	7	1.04	1.09	8.94
2,6-Xylenol	Ps	17	2.79	2.89	3.69
3,4-Xylenol	Ps	19	3.50	3.57	5.36
	denl	7	0.82	0.87	8.23
-----    Indanols    -----					
1-Indanol	Ps	6	2.65	2.38	-
	denl	6	1.84	1.34	-
2-Indanol	Ps	10	10.4	10.3	22.8
	denl	10	2.33	2.12	28.5
4-Indanol	Ps	12	4.58	4.62	4.84
	denl	12	0.70	0.65	3.06
5-Indanol	Ps	11	5.41	5.39	9.78
	denl	12	1.46	1.41	3.66
-----    Ethers    -----					
Dimethyl Ether	Ps	17	0.62	0.60	2.60
	denl	19	3.62	3.30	5.80
	denv	19	1.57	2.02	4.40

Table 4.3 (continued)

Compound	Prop.	No. of points	eq. 13	AARD%	
				eqs. 13&14	3PCS-MBWR
Methyl Ethyl Ether	Ps	18	1.29	0.85	1.98
	denl	17	0.85	1.14	1.20
	denv	18	13.4	13.1	13.6
Diethyl Ether	Ps	24	2.67	2.42	0.89
	denl	23	5.29	5.30	5.33
	denv	23	3.62	3.72	2.92
Ethyl Propyl Ether	Ps	17	2.20	0.78	2.20
	denl	18	3.46	2.43	2.10
Diphenyl Ether	Ps	13	0.41	0.39	1.62
	denl	23	6.22	6.03	6.24
-----    Ketones    -----					
Acetone	Ps	20	0.92	0.40	4.78
	denl	20	4.30	3.50	3.42
	denv	20	12.4	13.1	14.2
2-Butanone	Ps	17	0.03	0.02	0.87
	denl	4	0.12	0.14	3.70
2-Pentanone	Ps	18	0.02	0.02	0.96
	denl	18	0.26	0.27	4.30
-----    Furans    -----					
Furan	Ps	25	2.71	1.94	8.10
	denv	20	6.71	0.91	9.58
Tetrahydrofuran	Ps	25	0.93	0.93	2.01
	denl	10	0.49	0.32	2.95
Dibenzofuran	Ps	19	3.97	1.54	6.40
	denl	42	3.52	1.07	6.40

Table 4.3 (continued)

Compound	Prop.	No. of points	AARD±		
			eq. 13	eqs. 13&14	3PCS-MBWR
Sulfur-Containing Compounds					
Methyl Mercaptan	Ps	21	0.96	1.10	1.15
	denl	21	1.59	2.15	1.92
Ethyl Mercaptan	Ps	21	1.27	1.15	1.37
	denl	21	1.23	1.42	1.48
	denv	21	14.8	15.7	19.0
Thiophene	Ps	29	2.44	2.46	5.15
	denl	15	1.39	1.33	5.92
Tetrahydrothiophene	Ps	33	4.69	5.03	4.69
	denl	9	3.12	2.54	0.65
Thianaphthene	Ps	27	0.43	0.45	2.07
Dibenzothiophene	Ps	19	3.07	3.08	3.74
Amines					
Methylamine	Ps	17	2.74	0.79	6.83
Ethylamine	Ps	18	0.27	0.21	0.61
Dimethylamine	Ps	18	0.40	0.27	4.60
Diethylamine	Ps	19	0.45	0.43	2.20
	denl	19	3.44	4.24	5.10
	denv	19	10.8	8.71	14.4
Aniline	Ps	30	2.69	2.55	2.42
	denl	31	3.73	4.16	6.38



Table 4.3 (continued)

Compound	Prop.	No. of points	AARD%		3PCS-MBWR
			eq. 13	eqs. 13&14	
-----  -----    Nitrogen-Containing Compounds    -----					
Pyridine	Ps	46	2.87	0.91	3.85
	den1	27	4.26	4.29	5.51
Quinoline	Ps	42	3.23	3.89	8.52
	den1	16	1.40	0.90	6.53
Isoquinoline	Ps	29	1.17	2.69	2.81
	den1	19	0.26	2.41	4.62
Carbazole	Ps	26	3.37	1.85	0.61
	den1	6	21.1	8.87	24.2
Acridine	Ps	25	2.36	2.29	8.29
	den1	12	0.66	0.57	4.20
-----    Other Compounds    -----					
Toluene	Ps	33	1.81	1.86	1.63
	den.	13	0.20	0.33	1.16
o-Xylene	Ps	42	0.82	0.87	0.99
	den.	59	0.38	0.37	1.46
Diphenylmethane	Ps	38	1.51	1.42	2.53
	den.	3	2.06	0.46	3.23
Acetic Acid	Ps	22	2.29	0.70	11.3
	den1	22	7.17	3.48	6.0

density data to determine  $d_1$ ,  $d_2$ , and  $d_3$ . The resultant parameters are listed in Table 4.4. As pointed out in section 3.1, the new sets of  $\omega_s$  are very similar to those obtained using the homomorph method, see Table 3.2. Property calculations were made, once again, using the new correlation. The results are, for most cases, similar to the first set of results, and are reported for comparison in Table 4.3. Notable improvements are observed for 1-butanol, furan, dibenzofuran, carbazole, and acetic acid. The overall AARD% for vapor pressure and density predictions are 1.8% and 2.6%, respectively. The prediction results are compared graphically with experimental data via P-V-T diagrams. The P-V-T behavior for water, phenol, and dibenzofuran are shown in Figures 1, 2, and 3, respectively. The plots of percent deviations in vapor-pressure predictions versus temperature are made for a few compounds to illustrate the degrees of bias (or lack of bias) of the predictions. Deviation plots for phenol and dibenzofuran are shown in Figures 4 and 5. These plots show that the deviations are generally scattered, showing a bias value close to zero. On the basis of the results obtained here, the  $\omega_s$  correlation, equation (14), is recommended for use with the proposed multiparameter corresponding-states correlation, equation (13). Subsequent calculations reported here are made using  $\omega_s$  values determined from equation (14).

Table 4.4

The Structure Factors Determined Using Equation (14),  
and the Polar/Associative Parameters.

Compound Name	$\omega_S$	$d_{1\mu}^*$	$d_{2\mu}^*$	$d_{3\mu}^*$
Water	0.008	1.0058	0.0139	-0.0140
Ammonia	0.0073	0.8674	-0.09867	-0.09835
Methanol	0.0856	1.9249	-0.5891	-0.6506
Ethanol	0.196	2.2386	-0.5515	-1.2474
Propanol	0.280	1.7877	-0.04771	-1.1204
1-Butanol	0.308	2.2099	-0.5887	-1.6412
1-Pentanol	0.357	1.9348	-0.6398	-1.4602
1-Hexanol	0.379	3.1451	-4.1887	-2.5925
Phenol	0.248	1.7598	-4.3681	-1.0150
m-Cresol	0.301	1.5140	-1.4857	-0.9977
o-Cresol	0.287	1.4198	-3.2124	-0.7504
p-Cresol	0.304	1.6897	-4.3418	-0.8161
2,3-Xylenol	0.292	1.8871	-3.5052	-1.3502
2,4-Xylenol	0.310	1.2708	-0.6234	-0.9453
2,5-Xylenol	0.342	1.6607	-2.3021	-1.1669
2,6-Xylenol	0.293	1.4359	-3.3215	-1.0121
3,4-Xylenol	0.330	1.9454	-2.2242	-1.3998
1-Indanol	0.725	0.7834	-0.1454	0.9126
2-Indanol	0.716	2.6420	-1.6042	-0.8841
4-Indanol	0.335	0.3555	0.2975	-0.0049
5-Indanol	0.333	-0.02068	0.3875	0.4546
Dimethyl Ether	0.163	0.2330	0.5088	-0.2470

Table 4.4 (Continued)

Compound Name	$\omega_S$	$d_1\mu^*$	$d_2\mu^*$	$d_3\mu^*$
Methyl Ethyl Ether	0.204	0.4005	-0.0867	-0.3311
Diethyl Ether	0.246	0.6012	-0.8423	-0.4255
Ethyl Propyl Ether	0.285	-0.04253	0.0933	0.06840
Diphenyl Ether	0.378	0.0368	-0.1984	0.2008
Acetone	0.099	0.9389	-0.6541	-0.1744
2-Butanone	0.176	0.2894	0.3693	0.1115
2-Pentanone	0.209	0.8500	-1.1109	-0.3312
Furan	0.178	-0.4425	1.5890	0.1643
Tetrahydrofuran	0.169	0.4294	-0.6281	-0.1672
Dibenzofuran	0.291	-1.0740	1.2526	1.0671
Methyl Mercaptan	0.127	0.0266	-0.0634	0.0966
Ethyl Mercaptan	0.160	0.1736	0.3561	-0.1584
Thiophene	0.196	0.2958	-0.5622	-0.2110
Tetrahydrothiophene	0.167	0.2015	0.3169	-0.1452
Thianaphthene	0.285	0.4855	-2.0343	-0.1916
Dibenzothiophene	0.327	0.9124	-2.2063	-0.6007
Methylamine	0.146	1.1326	-0.2150	-0.9510
Ethylamine	0.181	0.7291	-0.4222	-0.4220
Dimethylamine	0.201	0.5199	0.3510	-0.3986
Diethylamine	0.258	-0.1130	1.1029	0.0108
Aniline	0.249	0.9222	-0.7013	-0.5315
Pyridine	0.155	0.3094	0.3251	-0.1749

Table 4.4 (Continued)

Compound Name	$\omega_s$	$d_{1u}^*$	$d_{2u}^*$	$d_{3u}^*$
Quinoline	0.230	-0.0613	1.3738	-0.1642
Isoquinolin	0.202	-0.3838	1.6982	0.1622
Carbazole	0.369	-1.4641	2.8509	1.0229
Acridine	0.332	-0.3281	0.5653	0.5771
Toluene	0.249	0.0380	0.1095	-.01673
o-Xylene	0.286	-.02118	0.2512	.05491
Diphenylmethane	0.423	0.2903	-0.7486	-.08933
Acetic Acid	0.250	0.5482	-1.3006	0.4567

FIGURE 2.  
EXPERIMENTAL AND PREDICTED SATURATION DENSITIES  
FOR PHENOL

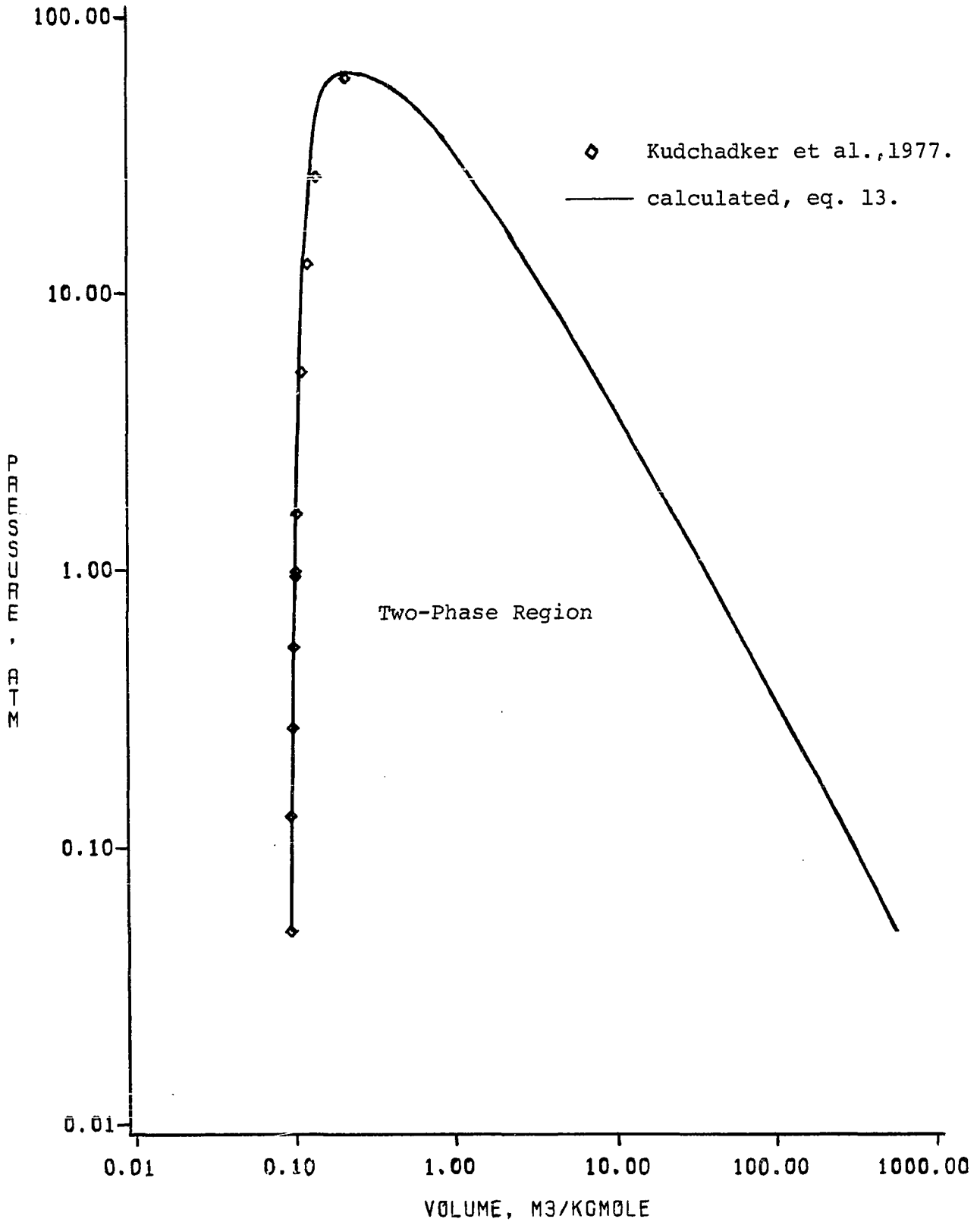


FIGURE 3.  
EXPERIMENTAL AND PREDICTED DENSITIES FOR  
DIBENZOFURAN

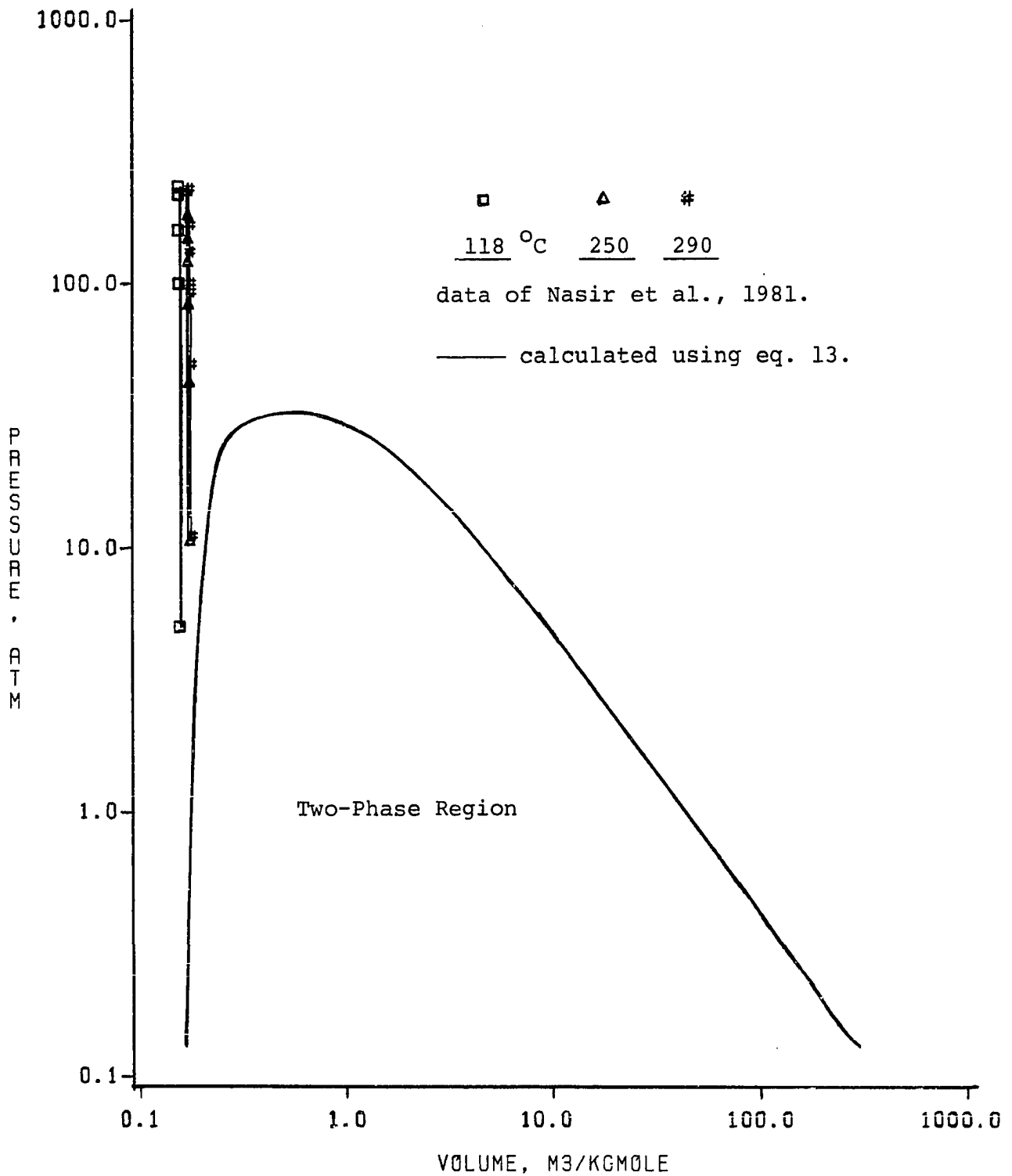


FIGURE 4.  
DEVIATIONS IN VAPOR-PRESSURE PREDICTIONS  
VS TEMPERATURE FOR PHENOL

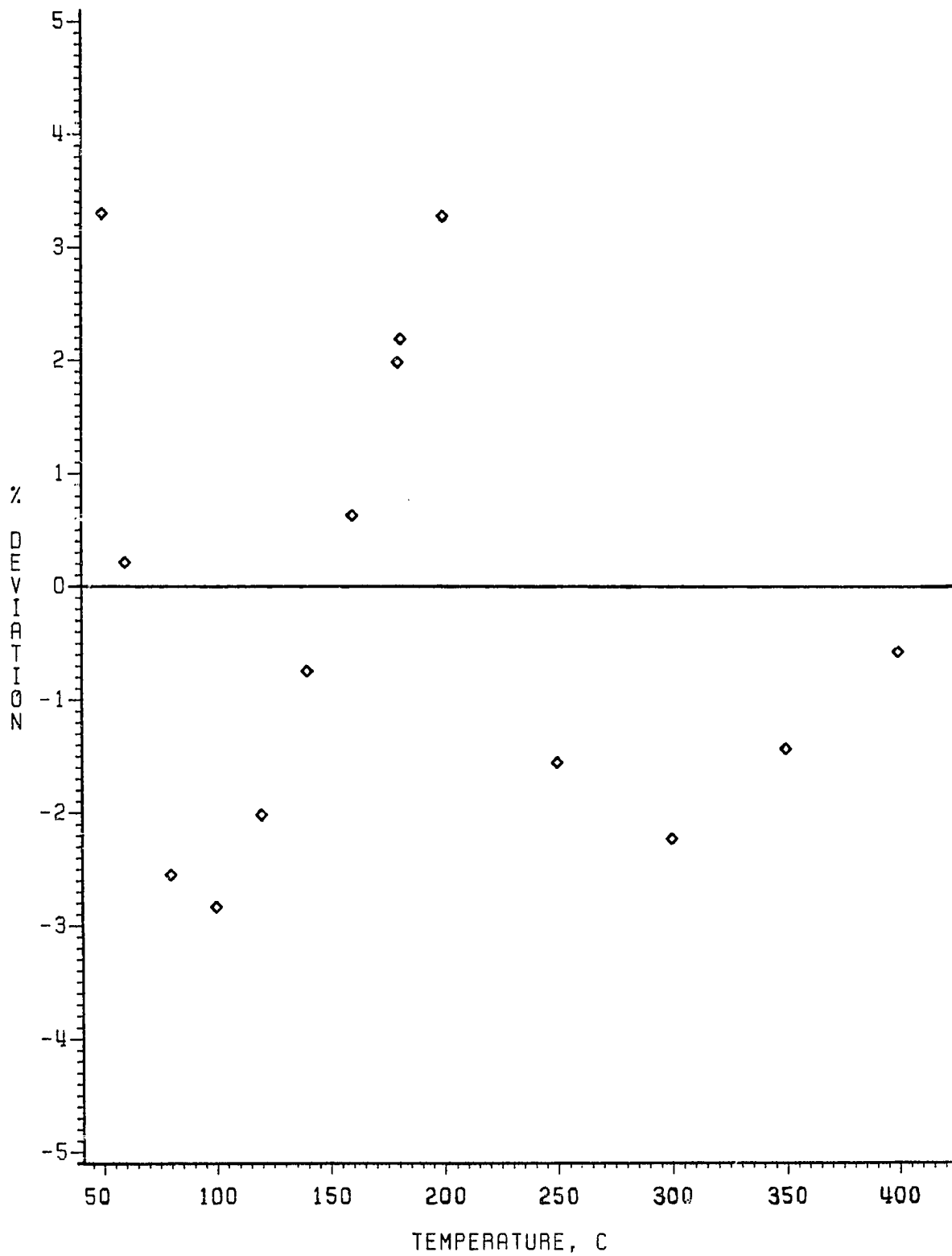
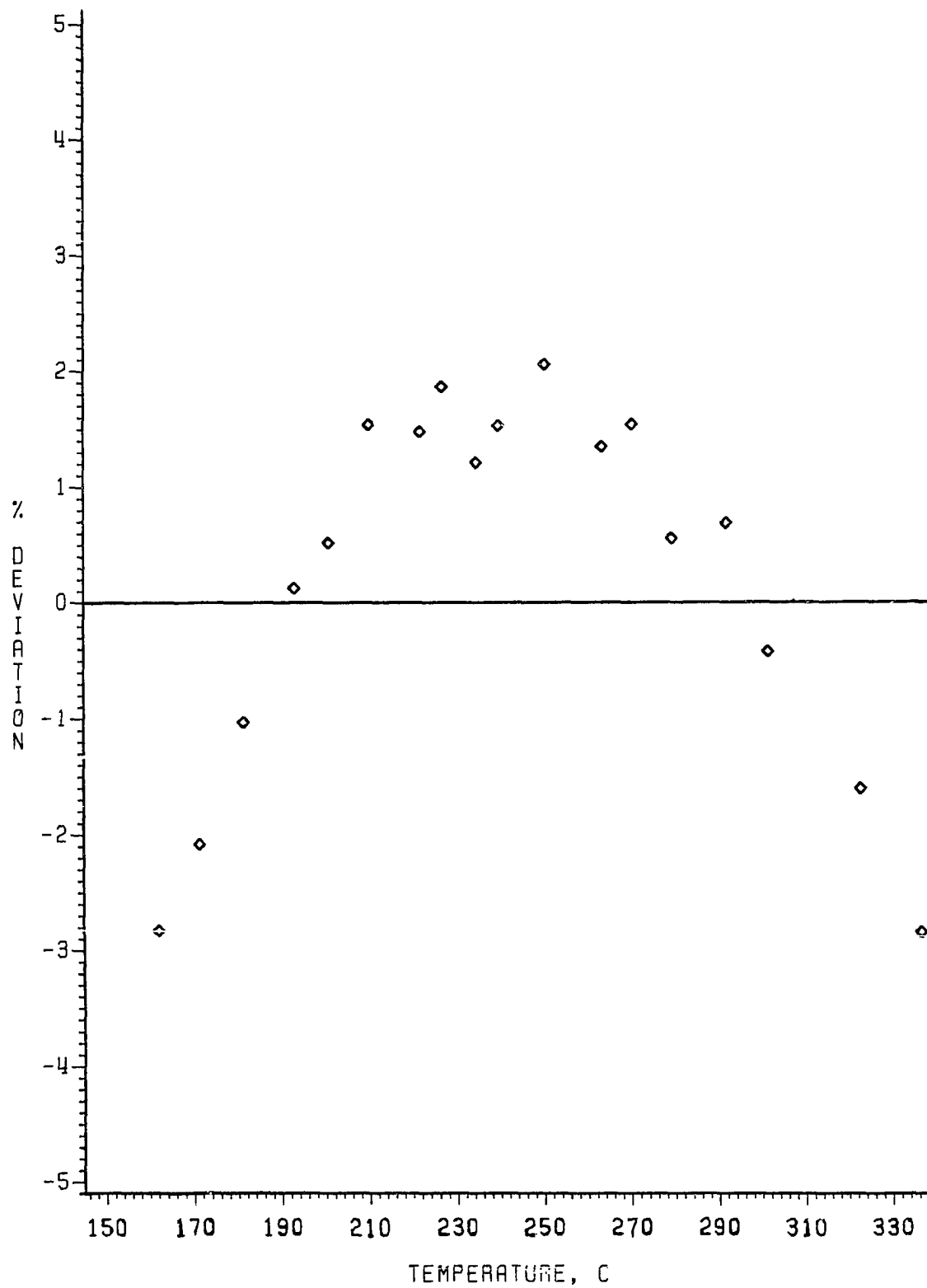




FIGURE 5.  
DEVIATIONS IN VAPOR-PRESSURE PREDICTIONS  
VS TEMPERATURE FOR DIBENZOFURAN



#### 4.4 Heat-of-Vaporization Predictions

To further test the new correlation, the polar/associative parameters,  $d_1$ ,  $d_2$ , and  $d_3$  determined using vapor pressure and density data, reported in Table 4.4, are used to predict enthalpy and enthalpy of vaporization for a number of polar and associating compounds. This is an important test because in order for the generalized correlation to be used effectively in process design, the correlation must be capable of predicting accurate vapor pressures, densities, and enthalpies for process-stream fluids. Equally important is that the temperature dependence of the correlation can be critically tested with the use of enthalpy data because the enthalpy expression, equation (25), contains the temperature derivative of compressibility  $Z$ . In general, enthalpy or enthalpy-departure data are used. However, enthalpy-of-vaporization data can be used if other enthalpy data are not available. If the enthalpy of vaporization can be predicted accurately, the enthalpies of both the vapor and liquid are predicted within reasonable levels of accuracy. For most compounds tested in this section, only enthalpy-of-vaporization data are available. Water and ammonia are the only compounds with enthalpy-departure data. The predicted enthalpy and enthalpy of vaporization deviate from the experimental values, averaged over all compounds, by 9.5 kJ/kg (4.1 Btu/lb). Results are reported in table 4.5. The

**Table 4.5**  
**Predictions of the Thermodynamic Properties Using**  
**Different Polar/Associative Parameters.**

Compound	Prop.	No. of points	AARD%		
			a	b	c
Water	Ps	64	0.57	-	11.9
	den.	385	1.46	-	6.47
	Hd	239	3.63	-	18.1
Ammonia	Ps	142	0.35	0.56	4.15
	den.	239	0.88	1.13	4.26
	Hd	145	2.85	2.10	8.95
-----    Phenols    -----					
Phenol	Ps	14	1.83	2.54	2.40
	denl	14	4.03	4.99	19.7
	H	14	7.50	7.38	6.94
m-Cresol	Ps	23	2.93	3.00	3.00
	denl	26	1.23	1.13	7.64
	H	23	6.46	6.31	8.23
o-Cresol	Ps	23	2.12	1.95	15.2
	denl	24	2.85	3.80	9.78
	H	23	7.27	7.46	6.97
p-Cresol	Ps	22	3.52	2.68	4.26
	denl	24	2.97	3.76	19.9
	H	22	6.20	5.42	7.74
2,3-Xylenol	Ps	19	3.61	4.28	4.67
	H	19	4.63	4.11	4.75
2,4-Xylenol	Ps	32	3.77	3.77	8.40
	denl	5	1.25	1.24	0.19
	H	19	3.36	3.31	5.30
2,5-Xylenol	Ps	18	4.63	4.63	5.57
	denl	7	1.09	0.32	8.91
	H	18	5.36	4.96	4.97
2,6-Xylenol	Ps	17	2.89	2.94	3.66
	H	18	2.16	2.12	3.42

Table 4.5 (continued)

Compound	Prop.	No. of points	AARD%		
			a	b	c
3,4-Xylenol	Ps	19	3.57	3.60	5.24
	denl	7	0.87	1.13	8.21
	H	19	5.43	5.08	6.02
-----    Indanols   -----					
1-Indanol	Ps	6	2.38	5.87	19.6
	denl	6	1.31	1.19	4.19
	H	6	34.6	26.4	5.60
2-Indanol	Ps	10	10.3	10.5	11.9
	denl	10	2.12	2.10	1.56
	H	10	18.2	15.9	10.3
4-Indanol	Ps	12	4.62	4.61	4.87
	denl	12	0.65	0.70	3.06
	H	12	1.48	1.43	2.27
5-Indanol	Ps	11	5.39	5.98	9.77
	denl	12	1.41	1.30	3.66
	H	11	7.21	5.61	1.88
-----    Furans   -----					
Furan	Ps	25	1.94	1.93	8.22
	denl	20	0.91	1.05	9.57
	H	25	2.30	2.28	4.74
Tetrahydrofuran	Ps	25	0.93	1.04	2.02
	denl	10	0.32	1.19	2.94
	H	24	2.99	2.23	2.01
-----    Sulfur-Containing Compounds   -----					
Thiophene	Ps	29	2.46	2.38	1.77
	denl	15	1.33	2.57	4.66
	H	28	2.16	2.08	1.85

Table 4.5 (continued)

Compound	Prop.	No. of points	AARD%		
			a	b	c
Tetrahydrothiophene	Ps	33	5.03	4.94	6.41
	denl	9	2.54	3.42	0.67
	H	24	5.73	5.54	5.34
-----    Nitrogen-Containing Compounds   -----					
Pyridine	Ps	46	0.91	0.94	3.92
	denl	27	4.29	3.78	5.51
	H	26	2.49	2.32	3.42
Quinoline	Ps	42	3.89	4.22	18.7
	denl	16	0.90	1.23	6.08
	H	23	7.35	7.45	7.02
Isoquinoline	Ps	29	2.69	2.74	7.64
	denl	19	2.41	2.04	6.98
	H	20	3.20	3.11	3.88
Carbazole	Ps	26	1.85	-	0.72
	denl	6	8.87	-	24.2
	H	10	2.89	-	6.02
Acridine	Ps	25	2.29	2.22	8.40
	denl	12	0.57	0.58	4.20
	H	15	5.40	5.37	8.01
Aniline	Ps	30	2.55	2.85	2.39
	denl	31	3.28	2.89	5.06
	H	29	4.86	4.77	5.36

Table 4.5 (continued)

- 
- a  
calculated using polar/associative parameters  
determined from vapor-pressure and density data  
(see Table 4.4).
- b  
Polar/associative parameters determined from vapor-  
pressure, density, and enthalpy of vaporization data.
- c  
Calculated by the 3PCS-MBWR correlation using the  
best orientation parameter, 1, determined from vapor-  
pressure, density, and enthalpy of vaporization data.

results show that parameters  $d_1$ ,  $d_2$ , and  $d_3$  determined using only vapor-pressure and density data can be used effectively in the calculation of enthalpy and enthalpy of vaporization.

To improve the enthalpy predictions, the polar/associative parameters,  $d_1$ ,  $d_2$ , and  $d_3$  are redetermined using vapor pressure, density, and enthalpy-of-vaporization data. With the new characterization parameters, vapor pressure, density, enthalpy, and enthalpy of vaporization are calculated. The average deviations for all compounds are reported in Table 4.5. In comparing these results to those obtained above using parameters from vapor pressure and density data only, no significant improvement in prediction accuracy for enthalpy of vaporization has been achieved by the inclusion of enthalpy-of-vaporization data in the data base. In fact, density predictions for some compounds actually deteriorate. It is considered best, therefore, to determine  $d_1$ ,  $d_2$ , and  $d_3$  using only vapor pressure and density data. The 3PCS-MBWR results are also given in Table 4.5 for comparisons.

## CHAPTER V

### SENSITIVITY OF THERMODYNAMIC-PROPERTY PREDICTIONS TO THE VALUES OF POLAR/ASSOCIATIVE PARAMETERS

From the results obtained for 51 polar and hydrogen-bonding compounds, as presented in Chapter IV, the new correlation is sufficiently accurate for use in process-design calculations. As discussed in section 4.2, the new correlation requires the use of  $T_c$ ,  $\rho_c$ ,  $\omega_s$ ,  $u^*$ ,  $d_1$ ,  $d_2$ , and  $d_3$  as characterization parameters. The first four parameters are either measurable, or can be calculated using correlations, see e.g., Brule et al., (1982). However, the polar/associative parameters  $d_1$ ,  $d_2$ , and  $d_3$  have to be determined from multiproperty regression analysis of vapor-pressure and density data. In chapter IV, all available vapor-pressure and density data were used to determine  $d_1$ ,  $d_2$ , and  $d_3$ .

In this chapter, data sets of different numbers of data points, and data sets consisting of different types of thermodynamic data are used to determine sets of  $d_1$ ,  $d_2$ , and  $d_3$ . These parameters are used to predict thermodynamic properties for the entire data set. The prediction



accuracies are then compared with those reported in chapter IV, e.g., Table 4.5. This study provides insight into sensitivity to the polar/associative parameters, and helps identify the types of thermodynamic property data most critical to the determination of the best set of parameters (Brule and Starling, 1982). Also, the minimum number of data points which are needed to determine a set of parameters that can be used to predict properties for the complete data set with reasonable accuracy will be identified. This study is particularly useful in the application of the correlation to undefined fractions since only a few inspection data are usually obtained for these fractions, e.g., boiling temperature (hence, vapor pressure), specific gravity, .... How well these few data points can be used to determine parameters that will ultimately be used to predict properties over wide ranges of temperature and pressure is of great interest to design engineers.

#### 5.1 Determination of Polar/Associative Parameters from a Small Set of Thermodynamic Data

For each compound studied in this section, a total of seven data points are selected. The three vapor-pressure and three density data points are at about 0.02, 0.2, and 1 bar. The enthalpy of vaporization datum is at 1 bar. These selected data are at very low pressures compared to the rest of the data which typically are at pressures up to the

critical pressure (see Table 4.2). These data are used in multiproperty regression analysis to determine polar/associative parameters,  $d_1$ ,  $d_2$ , and  $d_3$ . The resultant parameters are then used to predict the entire data set for vapor pressure, density, and enthalpy of vaporization. The results are compared in Table 5.1 with those obtained using parameters determined from the entire vapor pressure and density data set (compare columns designated a and b). For all practical purposes, both prediction results are equivalent, indicating that parameters determined using low-pressure data are as good as those determined using the entire data set covering much broader temperature and pressure ranges.

Results in section 4.5 indicate that enthalpy of vaporization data are not important in the determination of polar/associative parameters. To reconfirm this observation, the parameters are determined using only three vapor-pressure and three density data points, omitting the single enthalpy-of-vaporization datum. Prediction results for the entire data set using these parameters are presented in Table 5.1, column c. No deterioration in the prediction accuracy is observed for any system studied. These results reconfirm that enthalpy-of-vaporization data are not necessary in the determination of parameters  $d_1$ ,  $d_2$ , and  $d_3$ .

In the next study, the number of data points used in the determination of  $d_1$ ,  $d_2$ , and  $d_3$  are reduced to three. Three vapor-pressure data points are used to determine the

Table 5.1

Predictions of Vapor Pressure, Density, and Enthalpy of Vaporization  
Using the Polar/Associative Parameters Determined from  
Small Number of Data Points.

Compound	Prop.	No. of points	AARD%					
			a	b	c	d	e	f
-----    Phenols    -----								
Phenol	Ps	14	1.83	2.86	2.66	2.81	2.87	2.84
	denl	14	4.03	3.01	3.07	5.38	3.32	3.34
	H	14	7.50	6.73	6.66	4.58	5.97	6.00
m-Cresol	Ps	23	2.93	3.67	3.69	8.42	3.22	3.10
	denl	26	1.23	2.32	2.34	2.26	2.62	2.62
	H	23	6.46	6.04	6.03	7.61	6.25	6.27
o-Cresol	Ps	23	2.12	2.42	2.46	-	1.98	-
	denl	24	2.85	3.18	3.22	-	4.10	-
	H	23	7.27	6.37	6.36	-	7.37	-
p-Cresol	Ps	22	3.52	3.87	3.91	0.69	3.25	3.99
	denl	24	2.97	3.11	3.08	6.79	3.36	5.00
	H	22	6.20	5.24	5.23	4.83	5.40	4.22
2,4-Xylenol	Ps	32	3.77	-	5.17	5.19	5.32	5.49
	denl	5	1.25	-	0.12	1.10	0.16	1.75
	H	19	3.36	-	4.02	4.14	4.06	4.31

Table 5.1 (continued)

Compound	Prop.	No. of points	AARD%					
			a	b	c	d	e	f
2,5-Xylenol	Ps	18	4.63	-	5.19	6.62	5.39	6.03
	denl	7	1.09	-	0.30	10.4	0.44	0.86
	H	18	5.36	-	5.06	5.78	5.29	5.79
2,6-Xylenol	Ps	17	2.89	-	-	2.79	-	-
	H	18	2.16	-	-	2.22	-	-
3,4-Xylenol	Ps	19	3.57	-	4.07	10.3	4.23	4.13
	denl	7	0.87	-	0.53	2.86	0.94	1.09
	H	19	5.43	-	5.25	7.58	5.28	5.67
			-----   Indanols   -----					
1-Indanol	Ps	6	2.38	12.7	2.81	2.00	3.39	-
	denl	6	1.31	5.22	1.29	5.06	2.18	-
	H	6	34.6	16.1	33.0	34.4	33.4	-
2-Indanol	Ps	10	10.3	11.5	11.5	13.0	13.4	-
	denl	10	2.12	1.68	1.70	13.8	2.20	-
	H	10	18.2	10.5	10.6	12.6	10.9	-
4-Indanol	Ps	12	4.62	4.68	4.65	1.80	4.83	-
	denl	12	0.65	0.58	0.59	12.9	0.60	-
	H	12	1.48	2.07	1.99	5.30	2.75	-
5-Indanol	Ps	11	5.39	7.96	-	3.06	8.48	-
	denl	12	1.41	1.11	-	15.7	1.22	-
	H	11	7.21	1.15	-	9.63	1.55	-

Table 5.1 (continued)

Compound	Prop.	No. of points	AARD%					
			a	b	c	d	e	f
-----    Furans    -----								
Furan	Ps	25	1.94	3.29	3.32	3.02	3.35	1.85
	denl	20	0.91	0.90	0.91	2.30	0.98	0.98
	H	25	2.30	2.84	2.86	3.41	2.96	2.23
Tetrahydrofuran	Ps	25	0.93	1.15	1.08	-	0.97	-
	denl	10	0.32	0.31	0.31	-	0.29	-
	H	24	2.99	2.28	2.31	-	2.32	-
Dibenzofuran	Ps	19	1.54	1.52	1.51	-	1.50	6.32
	denl	42	1.07	1.09	1.08	-	2.16	1.07
-----    Sulfur-Containing Compounds    -----								
Thiophene	Ps	29	2.46	2.57	2.61	-	2.50	3.08
	denl	15	1.33	0.14	0.14	-	0.19	2.11
	H	28	2.16	2.07	2.06	-	2.15	2.46
Tetrahydrothiophene	Ps	33	5.03	5.76	5.78	5.29	5.51	9.26
	denl	9	2.54	0.75	0.75	3.05	1.46	3.97
	H	24	5.73	4.24	4.24	4.03	4.14	8.59

Table 5.1 (continued)

Compound	Prop.	No. of points	AARD%					
			a	b	c	d	e	f
-----								
-----								
Nitrogen-Containing Compounds								
-----								
Pyridine	Ps	46	0.91	0.95	0.97	-	0.98	7.46
	denl	27	4.29	4.25	4.24	-	4.09	1.68
	H	26	2.49	2.31	2.32	-	2.35	9.57
Quinoline	Ps	42	3.89	4.56	4.84	5.13	5.35	5.65
	denl	16	0.90	1.02	1.17	8.56	0.67	0.61
	H	23	7.35	7.19	7.25	7.11	7.32	7.14
Isoquinoline	Ps	29	2.69	4.76	3.16	3.50	3.19	11.5
	denl	19	2.41	0.48	0.63	0.64	0.85	0.41
	H	20	3.20	4.46	2.58	2.57	2.59	9.85
Acridine	Ps	25	2.29	3.84	3.48	1.79	3.67	12.2
	denl	12	0.57	0.56	0.52	6.62	0.75	2.00
	H	15	5.40	6.21	6.08	3.61	6.25	8.08
Aniline	Ps	30	2.55	4.87	4.88	4.53	4.95	5.36
	denl	31	3.28	2.05	2.04	3.93	2.03	2.85
	H	29	4.86	6.09	6.09	5.83	6.15	6.43
-----								
Average	Ps	504	3.00	3.70	3.74	-	3.78	5.77
	denl	342	2.01	1.75	1.72	-	2.01	2.08
	H	403	4.93	4.49	4.40	-	4.54	5.67

Table 5.1 (continued)

---

- a calculated using polar/associative parameters determined from the entire vapor-pressure and density data (see Table 4.4), used herein as bases for comparisons.
- b Polar/associative parameters determined from 3 vapor-pressure, 3 density, and 1 enthalpy-of-vaporization data.
- c Polar/associative parameters determined from 3 vapor-pressure, and 3 density data.
- d Polar/associative parameters determined from 3 vapor-pressure data.
- e Polar/associative parameters determined from 2 vapor-pressure, and 1 density data.
- f Polar/associative parameters determined from 1 vapor-pressure and 2 density data.

parameters. Prediction results for the entire data set using these parameters are presented in Table 5.1, column d. Most of the vapor-pressure predictions are comparable to the previous cases, see e.g., column c, with a few exceptions. However, density predictions deteriorate significantly, e.g., for 2,5-xyleneol, the density AARD% is 10.4 % compared to 0.30 % in column c. It is evident that vapor-pressure data alone is not sufficient in determining the parameters. Both vapor pressure and density data are required in obtaining an optimum set of parameters  $d_1$ ,  $d_2$ , and  $d_3$ . Therefore, new sets of data each containing two vapor-pressure points (at 0.02 and 1 bar) and one density point (at 1 bar) are created. Parameters are then determined using these three data points. The resultant parameters are again used to predict properties for the entire data set. Prediction results are presented in Table 5.1, column e. Comparing column e (2 Ps, 1 den.) with column c (3 Ps, 3 den.), for most systems studied, the prediction accuracies for both cases are about the same. However, density-prediction errors of a few systems, e.g., dibenzofuran, and 4-indanol for the case in column e are slightly larger than those in column c. The differences are generally small and do not affect other property calculations. These results indicate that a minimum of three data points, consisting of two vapor-pressure data and one density datum, are all that are needed in determining the optimum parameters  $d_1$ ,  $d_2$ , and  $d_3$ . However, for undefined fractions, there is generally



only 1 vapor-pressure datum available, but more than one density data may be available (or can be easily measured). Therefore, a more critical test is to use one vapor-pressure datum and two density data in the determination of  $d_1$ ,  $d_2$ , and  $d_3$ .

New sets of data each containing one vapor-pressure datum (at 1 bar) and two density data points (at 0.8 and 1 bar) were created. Parameters are then determined using these three data points. The resultant parameters are again used to predict properties for the entire data set. Prediction results are presented in Table 5.1, column f. In this case, the vapor-pressure prediction accuracies for some compounds deteriorate significantly, while the density prediction accuracies for most compounds remain practically unchanged. Examination of the vapor-pressure calculation results reveal that large deviations occur in the low pressure region, e.g., at 0.01 bar, as shown in Table 5.2 for isoquinoline. However, vapor-pressure prediction accuracies at high pressures are generally satisfactory. The parameters determined using vapor-pressure data at 1 bar cannot be used reliably to calculate vapor pressure at much lower temperatures, but are reasonably reliable at high temperatures. Comparing these results with the previous case (2 Ps and 1 den.), it is evident that vapor-pressure data at low temperatures are essential in the determination of parameters  $d_1$ ,  $d_2$ , and  $d_3$ . For pure compounds, these data are generally available. Unfortunately, for undefined

Table 5.2

Detailed Calculations of Thermodynamic Properties for Isoquinoline  
Using Polar/Associative Parameters Determined  
from One Vapor-Pressure Datum and Two Density data.

prop.: Viswanath & Wilhoit 1979.

-----characterization parameters-----

	mw	tc K	vc cc/mol	ws	u*
input :	129.161	803.15	403.00	0.214	0.446

-----polar/associative parameters-----

input :	.16364	1.08580	-.31190
---------	--------	---------	---------

temp °C	pres atm	-----property-----					ref
		code	expm	calc	aad	%aad	
60.00		4	.001	.001	.000	-35.182	1
70.00		4	.002	.001	-.001	-34.053	1
80.00		4	.004	.002	-.001	-32.261	1
90.00		4	.006	.004	-.002	-29.997	1
100.00		4	.010	.007	-.003	-27.387	1
110.00		4	.015	.012	-.004	-24.610	1
120.00		4	.024	.019	-.005	-21.865	1
130.00		4	.036	.029	-.007	-19.163	1
140.00		4	.052	.043	-.009	-16.554	1
150.00		4	.075	.064	-.011	-14.111	1
160.00		4	.105	.093	-.012	-11.830	1
170.00		4	.145	.131	-.014	-9.778	1
180.00		4	.198	.182	-.016	-7.859	1
190.00		4	.265	.249	-.016	-6.204	1
200.00		4	.349	.333	-.017	-4.749	1
220.00		4	.585	.571	-.014	-2.418	1
240.00		4	.937	.929	-.008	-.849	1
260.00		4	1.440	1.441	.001	.094	1
280.00		4	2.142	2.148	.006	.283	1
300.00		4	3.079	3.089	.010	.328	1
320.00		4	4.303	4.309	.007	.151	1
340.00		4	5.882	5.853	-.029	-.486	1
360.00		4	7.866	7.766	-.100	-1.273	1
380.00		4	10.264	10.095	-.169	-1.650	1
400.00		4	13.225	12.887	-.338	-2.556	1
440.00		4	21.021	20.071	-.950	-4.519	1
480.00		4	31.483	29.767	-1.716	-5.451	1
520.00		4	45.398	42.336	-3.063	-6.746	1
530.00		4	49.149	46.179	-2.970	-6.042	1

Table 5.2 (continued)

temp °C	pres atm	-----property-----					
		code	expm	calc	aad	%aad	ref
60.00	.001	1	1.067	1.053	-.014	-1.352	1
70.00	.002	1	1.059	1.047	-.012	-1.162	1
80.00	.004	1	1.051	1.041	-.010	-.984	1
90.00	.006	1	1.044	1.034	-.010	-.915	1
100.00	.010	1	1.036	1.028	-.008	-.768	1
110.00	.015	1	1.028	1.021	-.007	-.636	1
120.00	.024	1	1.019	1.015	-.004	-.424	1
130.00	.036	1	1.011	1.008	-.003	-.327	1
140.00	.052	1	1.003	1.001	-.002	-.247	1
150.00	.075	1	.995	.993	-.002	-.187	1
160.00	.105	1	.987	.986	-.001	-.146	1
160.00	.105	1	.987	.986	-.001	-.146	1
170.00	.145	1	.978	.978	.000	-.022	1
180.00	.198	1	.970	.970	.000	-.020	1
190.00	.265	1	.962	.962	.000	-.038	1
200.00	.349	1	.953	.953	.000	.029	1
220.00	.585	1	.936	.936	.000	.000	1
240.00	.937	1	.918	.918	.000	.000	1
260.00	1.440	1	.899	.899	.000	.032	1
60.00	.001	5	196.719	200.072	3.353	1.705	1
70.00	.002	5	192.725	200.022	7.297	3.786	1
80.00	.004	5	189.063	199.439	10.376	5.488	1
90.00	.006	5	185.735	198.424	12.690	6.832	1
100.00	.010	5	182.406	197.058	14.652	8.033	1
110.00	.015	5	180.409	195.405	14.996	8.312	1
120.00	.024	5	178.412	193.518	15.106	8.467	1
130.00	.036	5	176.415	191.438	15.024	8.516	1
140.00	.052	5	174.750	189.202	14.451	8.270	1
150.00	.075	5	172.753	186.836	14.083	8.152	1
160.00	.105	5	171.089	184.364	13.275	7.759	1
170.00	.145	5	169.425	181.804	12.380	7.307	1
180.00	.198	5	167.760	179.173	11.412	6.803	1
190.00	.265	5	166.096	176.482	10.386	6.253	1
200.00	.349	5	164.432	173.742	9.310	5.662	1
220.00	.585	5	161.103	168.145	7.042	4.371	1
240.00	.937	5	157.775	162.431	4.656	2.951	1
260.00	1.440	5	154.113	156.623	2.510	1.629	1
280.00	2.142	5	150.452	150.722	.270	.180	1
300.00	3.079	5	146.457	144.732	-1.725	-1.178	1

Table 5.2 (continued)

-----SUMMARY-----			
code	property	units	prediction deviations
1	liquid density	gm/cc	.39 %aad for 19 points
4	vapor pressure	atm	11.33 %aad for 29 points
5	heat of vaporization	Btu/lb	9.75 aad for 20 points

fractions, the inspection data normally measured for the fractions are the normal boiling point and specific gravities. As the results in this section indicate, the parameters determined using the inspection data for the fractions cannot be used to predict accurately the vapor-pressure (volatility data) of the fractions at temperatures much lower than the average normal boiling point. The densities, on the other hand, can be predicted with greater confidence over wide temperature and pressure ranges. Since the errors in vapor-pressure calculations may have adverse effects on the k-value calculations for the fractions, the problems encountered here must be examined further. One obvious solution is to measure vapor pressure (volatility) for the fraction at a temperature lower than the normal boiling point. This measurement can be done for fractions that are used in detailed laboratory study, e.g., Wilson et al., (1981), but is not practical for routine inspection data measurements. Another possible solution is to reduce the number of parameters ( $d_1$ ,  $d_2$ , and  $d_3$ ) that have to be determined from data by correlating some of the parameters as a function of measurable quantities. The reduction of the number of characterization parameters is very desirable in light of the difficulties encountered for the undefined fractions. Work in this area is in progress. If  $d_1$ ,  $d_2$ , and  $d_3$  can all be correlated as functions of measurable quantities, the equation-of-state correlation will be totally generalized in that  $d_1$ ,  $d_2$ , and  $d_3$  are no longer

component specific, but are determined from a set of universal constants. The work on further generalization of the correlation is recommended.

## 5.2 Application of the Correlation to Some Undefined Coal-Fluid Fractions.

In this section, the new correlation is applied to predict the density for coal-fluid fractions. Density measurements have been made for several wide-boiling coal-fluid fractions from the Exxon-Donor-Solvent (EDS) process over wide ranges of temperature and pressure (Hwang et al., 1982). For each fraction,  $T_c$  and  $V_c$  are calculated using the correlations of Brulé et al., (1982). The structure factor,  $\omega_s$ , is calculated using equation (14). The dipole moment is calculated using the correlation of Owens (1982). As pointed out in section 5.1, densities for the fractions can be reliably predicted using parameters  $\bar{d}_1$ ,  $\bar{d}_2$ , and  $\bar{d}_3$  determined from inspection data. Therefore, the polar/associative parameters  $d_1$ ,  $d_2$ , and  $d_3$  are determined via multiproperty regression analysis of the average-normal-boiling point for the fraction (vapor pressure), and two density data. The resultant parameters are used to predict the entire density data set for the fraction. Results are reported in Table 5.3. Generally, the predictions accuracy are satisfactory. Note that the reduced dipole moment values for most of the fractions are small, indicating that the fractions are not very polar.

Table 5.3

Comparisons of Exxon Coal-Fluid Density Data with Predictions  
by the New Correlation, and by the 3PCS-MBWR Correlation  
Data of Hwang et al., 1982.

Exxon Coal <sup>1</sup> Liquid	Avg MW	Tb Range °C	Avg Tb °C	Range		N	$\mu^*$	%AARD	
				T, °C	P, kPa			Eq. 13	3PCS <sup>2</sup>
IHS	179	202-513	271	24-454	69-138	33	0.08	1.51	1.04
IA-3	167	121-524	246	44-424	23-205	30	0.24	0.63	4.18
IA-6	172	193-421	260	22-428	23-205	36	0.04	0.39	1.05
IA-10	164	116-421	244	43-429	23-205	32	0.01	1.17	1.58
WV-1	192	177-429	276	21-371	14-207	26	0.17	0.20	4.40

1

I = Illinois No. 6 Coal; W = Wyoming Wyodak Coal

2

The 3PCS-MBWR results taken from Brulé et al., 1982.

Therefore, the 3PCS-MBWR correlation is applicable to these fractions as well. The density prediction results using the 3PCS-MBWR correlation, as reported by Brulé et al., (1982), are given in Table 5.3 for comparison.



## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

A multiparameter corresponding-states equation of state has been developed for accurate predictions of thermodynamic properties of pure nonpolar, polar, and associating fluids. The correlation can be divided into a nonpolar and a polar/associating contributions. The nonpolar contribution comes from the three-parameter corresponding-states correlation. The polar/associating contribution is determined from the water equation of state. The nonpolar and water equation are generalized for polar and associating compounds by using reduced dipole moment, and a temperature- and density-dependent polar/associative factor. The characterization parameters required are critical temperature, critical density, structure factor, reduced dipole moment, and three polar/associating parameters. The first four parameters are either measurable quantities or can be calculated using correlations, while the last three must be determined from experimental data. Characterization parameters are given for 51 polar and associating compounds.

The correlation was applied with satisfactory results to a wide variety of nonpolar, polar, and associating compounds including naphthalene, tetralin, water, ammonia, straight-chain alcohols, amines, ethers, ketones, phenols, indanols, quinoline, thiophene, dibenzofuran, acridine, and many other nitrogen-, oxygen-, and sulfur-containing model coal compounds. For 51 polar and associating compounds, the average absolute deviations are 1.8% for vapor pressure, 2.6% for density, and 9.5 kJ/kg (4.1 Btu/lb) for enthalpy and enthalpy of vaporization.

The sensitivity of the thermodynamic-property predictions to the values of polar/associative parameters were examined. It was demonstrated that the polar/associative parameters can be determined effectively using small number of vapor-pressure and density data. Both vapor pressure and density data are needed to determine an optimum set of parameters. It was further shown that two vapor-pressure data, and one density datum are all that is needed to determine the parameters. As a result, the correlation can be applied readily to pure compounds with few experimental data. Parameters determined using one vapor-pressure datum and two density data can be used to reliably predict the densities, but not the vapor pressures at low temperatures. As a result, the densities for undefined fractions can be predicted with reasonable levels of accuracy, provided measurements of the fraction boiling point, molecular weight and density (at two temperatures)

are available. In order to predict the vapor pressure (volatility) for the fractions, an additional vapor pressure datum at a temperature lower than the normal-boiling point is required.

The correlation was applied to predict the density for several wide-boiling coal-fluid fractions from the Exxon-Donor-Solvent process with reasonable accuracy.

It is recommended that the number of polar/associative parameters be reduced via correlation for the parameters and that the equation-of-state correlation be further generalized so that the characterization parameters may be more conveniently and reliably obtained for undefined fractions.

## NOMENCLATURE

### Roman

$E_i$	generalized $i$ th equation-of-state parameter
$a_i, b_i, c_i$	universal constants in expression for $E_i$
$d_1, d_2, d_3$	polar/associative characterization parameters
den.	density (vapor and liquid)
denl	liquid density
denv	vapor density
$f$	pure component fugacity
$F_\alpha$	polar/association factor
$H - H^0$	enthalpy departure of fluid
$k$	Boltzmann constant ( $1.38054 \times 10^{-23} \text{J/K}$ )
$P$	absolute pressure
$P_s$	vapor pressure
$T$	absolute temperature
$T^*$	reduced temperature
$T_b$	normal boiling temperature
$T_c$	critical temperature
$V_c$	critical volume
$Z$	compressibility factor
$Z_o$	isotropic-reference-fluid compressibility factor

$Z_\gamma$	shape contribution to compressibility factor
$Z_\alpha$	polar and associative contribution to compressibility factor

### Greek

$\alpha$	association parameter
$\epsilon$	characteristic molecular-energy parameter
$\gamma$	molecular orientation parameter
$\mu$	dipole moment, debye
$\mu^*$	reduced dipole moment
$\rho$	density
$\rho^*$	reduced density
$\omega$	acentric factor
$\omega_S$	structure factor
$\sigma^3$	characteristic molecular-size parameter

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## APPENDIX A

### EXPRESSIONS FOR DERIVED THERMODYNAMIC PROPERTIES

The classical relationships for the enthalpy departure of a pure compound is given by:

$$H-H^0 = RT(Z-1) + \int_0^{\rho} \{P - T(\partial P/\partial T)_\rho\} d\rho/\rho^2 \quad (A.1)$$

In terms of the reduced temperature  $T^*$ , the reduced density  $\rho^*$ , and the compressibility factor  $Z$ , equation A.1 becomes

$$H-H^0 = RT(Z-1) - \frac{\epsilon RT^*}{k} \int_0^{\rho^*} (\partial Z/\partial T^*)_{\rho^*} d \ln \rho^* \quad (A.2)$$

Substituting  $Z$  from equation (22) into equation A.2,

$$\begin{aligned} H-H^0 = & RT(Z-1) - \frac{\epsilon}{k} RT^*{}^2 \{ \rho^* \{ E_2 T^{*-2} + 3E_3 T^{*-4} - 4E_9 T^{*-5} + \\ & 5E_{11} T^{*-6} + \mu^* d_3 (c_1 - c_2 T^{*-1} - c_3 T^{*-3} + c_9 T^{*-4}) \} + \\ & \frac{1}{2} \rho^*{}^2 \{ E_6 T^{*-2} + 2E_{10} T^{*-3} + \mu^* d_3 (c_5 - c_6 T^{*-1}) \} + \\ & \frac{1}{5} \rho^*{}^5 \{ -E_7 T^{*-2} - 2E_{12} T^{*-3} + \mu^* d_3 (c_{15} + c_7 T^{*-1} + \\ & \qquad \qquad \qquad c_{12} T^{*-2}) \} - \\ & \frac{1}{3} \rho^*{}^3 \mu^* \{ 2d_2 (c_2 T^{*-2} + 3c_3 T^{*-4} - 4c_9 T^{*-5}) + \\ & \qquad \qquad \qquad 2(d_1 + 3/5 d_2 \rho^*{}^2) c_{13} T^{*-3} + d_3 c_{13} T^{*-2} \} - \\ & \frac{1}{4} \rho^*{}^4 \mu^* T^{*-2} \{ d_2 c_6 + (d_1 + 2/3 d_2 \rho^*{}^2) c_{14} \} - \end{aligned}$$

$$\begin{aligned}
& 1/6\rho^* \mu^* T^{*-2} \{ (d_1 + 3/4 d_2 \rho^{*2}) c_{16} \} + \\
& 2/35\rho^* \mu^* T^{*-2} \{ d_2 (c_7 + 2c_{12} T^{*-1}) \} - \\
& \left\{ \frac{e^{-E_4 \rho^{*2}}}{2E_4} (2 + E_4 \rho^{*2}) - \frac{1}{E_4} \right\} \{ T^{*-4} (-3E_8 + \mu^* d_3 T^* c_8 + 3\mu^* d_2 \rho^{*2} c_8) + \\
& 3\mu^* d_2 c_8 T^{*-4} \{ e^{-E_4 \rho^{*2}} (3 + 3E_4 \rho^{*2} + E_4^2 \rho^{*4}) - 3 \} / (2E_4^2) \} \quad (A.3)
\end{aligned}$$

The fugacity expression is:

$$\begin{aligned}
\ln (f/P) &= \int_0^{\rho^*} (Z-1) d \ln \rho^* - \ln Z + (Z-1) \\
&= (Z-1) - \ln Z + \rho^* \{ E_1 - E_2 T^{*-1} - E_3 T^{*-3} + E_9 T^{*-4} - \\
& E_{11} T^{*-5} \} + \frac{1}{2} \rho^{*2} \{ E_5 - E_6 T^{*-1} - E_{10} T^{*-2} \} + \\
& 1/5 \rho^{*5} \{ E_{15} + E_7 T^{*-1} + E_{12} T^{*-2} \} + 1/3 \rho^{*3} E_{13} T^{*-2} + \\
& 1/4 \rho^{*4} E_{14} T^{*-1} + 1/6 \rho^{*6} E_{16} T^{*-1} - \\
& \mu^* d_2 \rho^{*2} \{ 2/3 \rho^* (c_1 - c_2 T^{*-1} - c_3 T^{*-3} + c_9 T^{*-4}) + \\
& 1/4 \rho^{*2} (c_5 - c_6 T^{*-1}) + 2/15 \rho^{*3} c_{13} T^{*-2} + \\
& 1/12 \rho^{*4} c_{14} T^{*-1} + 1/12 \rho^{*4} c_{14} T^{*-1} + 2/35 \rho^{*5} (c_{15} + \\
& c_7 T^{*-1} + c_{12} T^{*-2}) + 1/24 \rho^{*6} c_{16} T^{*-1} \} -
\end{aligned}$$

$$\begin{aligned}
& (1/2E_4) \{ e^{-E_4 \rho^{*2}} (2 + E_4 \rho^{*2}) - 2E_4 \} \{ E_8 T^{*-3} - \mu^* d_2 \rho^{*2} c_8 T^{*-3} \} - \\
& (1/2E_4^2) (\mu^* d_2 c_8 T^{*-3}) \{ e^{-E_4 \rho^{*2}} (3 + 3E_4 \rho^{*2} + E_4^2 \rho^{*4}) - 3 \} \quad (A.4)
\end{aligned}$$

## APPENDIX B

### SOURCE LISTING OF EQUATION OF STATE FUNCTION SUBROUTINES

```

function enth(t,rho)
c . calculate enthalpy departure at given temperature and density
common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
1 ,a(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
rhos=0.3189*rho/rhoc
tstar=1.2593*t/tcrit
rt=rgas*t
enth=-rt*tstar*fi2(t,rho)+rt*(pres(t,rho)/rgas/t/rho-1.0)
return
end

function fugcof(t,rho)
c . calculate fugacity at given temperature and density
common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
1 ,a(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
fp=log(rho*rgas*t)+fi1(t,rho)+(pres(t,rho)/rho/rgas/t-1.0)
fugcof=exp(fp)
return
end

function pres(t,rho)
c . calculate pressure at given temperature and density
common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
1 ,a(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
common /gwater/wh2o
dimension ai(12), bi(12), ac(12)
w=a(2)
wh2o=0.008
rhos=0.3189*rho/rhoc
tstar=1.2593*t/tcrit
t4=4.86121
x=1./tstar
x2=x*x
x3=x2*x
x4=x3*x
x5=x4*x

```

```

call acalc(ac,w)
tm1=ac(1)-ac(2)*x-ac(3)*x3+ac(9)*x4-ac(11)*x5
tm2=ac(5)-ac(6)*x-ac(10)*x2
tm3=ac(7)*x+ac(12)*x2
tm4=ac(8)*x3
tme=(1.+t4*rhos**2)*(exp(-t4*rhos**2))
tm4=tme*tm4*(rhos**2)
z1=1.+rhos*tm1+tm2*rhos**2
z2=tm3*rhos**5+tm4
za=zwater(t,rho)
z=z1+z2+(a(1)+a(3)*rhos*rhos+a(5)/x)*za
pres=z*rho*rgas*t
return
end

```

```

c
function zwater(t,rho)
. calculate Za
common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
1 ,ax(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
common /gwater/wh2o
dimension a(16)
rhos=0.3189*rho/rhoc
tstar=1.2593*t/tcrit
t4=4.86121
x=1./tstar
x2=x*x
x3=x2*x
x4=x3*x
x5=x4*x
call rcalc(a)
tm1=a(1)-a(2)*x-a(3)*x3+a(9)*x4
tm2=a(5)-a(6)*x
tm3=a(7)*x+a(12)*x2+a(15)
tm4=a(8)*x3
tmn=a(13)*x2
tmo=a(14)*x
tmp=a(16)*x
tme=(1.+t4*rhos**2)*(exp(-t4*rhos**2))
tm4=tme*tm4*(rhos**2)
z1=rhos*tm1+tm2*rhos**2
z2=tm3*rhos**5+tm4
z3=rhos*rhos*rhos*tmn
z4=rhos*rhos*rhos*rhos*tmo
z5=rhos*rhos*rhos*rhos*rhos*tmp
zwater=z1+z2+z3+z4+z5
return
end

```

```

subroutine acalc(ci,w)
c  . calculate 3PCS-MBWR coefficient, ai+bi*gamma
dimension ai(12), bi(12), ci(12)
data ai/1.45907,4.98813,2.20704,4.86121,4.59311,
1 5.06707,11.4871,9.22469,.094624,1.48858,.015273,
2 3.51486/
data bi /.32872,-2.64399,11.3293,0.0,2.79979,10.3901,
1 10.3730,20.5388,2.7601,-3.11349,.18915,.94260/
ci(1)=ai(1)+bi(1)*w
ci(2)=ai(2)+bi(2)*w
ci(3)=ai(3)+bi(3)*w
ci(4)=ai(4)
ci(5)=ai(5)+bi(5)*w
ci(6)=ai(6)+bi(6)*w
ci(7)=ai(7)+bi(7)*w
ci(8)=ai(8)+bi(8)*w
ci(9)=ai(9)+bi(9)*w
ci(10)=ai(10)+bi(10)*w
ci(11)=ai(11)+bi(11)*w
ci(12)=ai(12)+bi(12)*w
return
end

```

```

subroutine rcalc(a)
c  . Constants for Za, taken from EOS for water
dimension a(16)
a(1)=0.485914
a(2)=-1.06672
a(3)=5.39716
a(4)=0.0
a(5)=-1.55842
a(6)=4.70204
a(7)=3.47628
a(8)=17.2603
a(9)=0.497917
a(10)=0.0
a(11)=0.0
a(12)=14.7689
a(13)=-1.79202
a(14)=4.78259
a(15)=7.46297
a(16)=-23.3345
return
end

```



```

function f11(t,rho)
c . evaluate integral f11 for fugacity calculations
common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
1 ,ax(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
dimension a(12),ri(16)
w=ax(2)
rhos=0.3189*rho/rhoc
tstar=1.2593*t/tcrit
t4=4.86121
x=1./tstar
x2=x*x
x3=x2*x
x4=x3*x
x5=x4*x
tm0=exp(-t4*rhos**2)
c . 3PCS-MBWR part
call acalc(a,w)
tm1=a(1)-a(2)*x-a(3)*x3+a(9)*x4-a(11)*x5

tm2=a(5)-a(6)*x-a(10)*x2
tm3=a(7)*x+a(12)*x2
t5 =a(8)*x3
tm4=t5/t4 - t5*tm0/t4
tm4=tm4-0.5*t5*(rhos**2)*tm0
f1=rhos*tm1+0.5*(rhos**2)*tm2
f2=0.2*tm3*(rhos**5)+tm4
c . association part (based on water)
call rcalc(ri)
tm1=ri(1)-ri(2)*x-ri(3)*x3+ri(9)*x4-ri(11)*x5
tm2=ri(5)-ri(6)*x-ri(10)*x2
tm3=ri(7)*x+ri(12)*x2+ri(15)
t5 =ri(8)*x3
tm4=t5/t4 - t5*tm0/t4
tm4=tm4-0.5*t5*(rhos**2)*tm0
tmn=ri(13)*x2
tmo=ri(14)*x
tmp=ri(16)*x
f3=rhos*tm1+0.5*(rhos**2)*tm2
f4=0.2*tm3*(rhos**5)+tm4
f5=1.0/3.0*rhos*rhos*rhos*tmn
f6=1.0/4.0*rhos*rhos*rhos*rhos*tmo
f7=1.0/6.0*rhos*rhos*rhos*rhos*rhos*rhos*tmp
c .
tm44=-t5*tm0*(t4*t4*rhos**4+3.0*t4*rhos*rhos+3.0)/
& 2.0/t4/t4+3.0*t5/2.0/t4/t4
f8=1.0/3.0*rhos*rhos*rhos*tm1+0.25*(rhos**4)*tm2
f9=1.0/7.0*tm3*(rhos**7)+tm44
f10=1.0/5.0*rhos*rhos*rhos*rhos*rhos*tmn
f11=1.0/6.0*rhos*rhos*rhos*rhos*rhos*rhos*tmo
f12=1.0/8.0*rhos*rhos*rhos*rhos*rhos*rhos*rhos*rhos*tmp
f11=f1+f2+(ax(1)+ax(5)/x)*(f3+f4+f5+f6+f7)
& +ax(3)*(f8+f9+f10+f11+f12)
return
end

```

```

function fi2(t,rho)
c . evaluate integral fi2 for enthalpy departure calculations
common /prm/rgas,renrgy,tcrit,pcrit,rhoc,w,alpha,beta,xmw
1 ,ax(40),b(7),nterms,nparm,numb,rtop,rmidl,rmidv
dimension a(12),ri(16)
w=ax(2)
rhos=0.3189*rho/rhoc
tstar=1.2593*t/tcrit
t4=4.86121
x=1./tstar
x2=x*x
x3=x2*x
x4=x3*x
x5=x4*x
x6=x5*x
tm0=exp(-t4*rhos**2)
c . 3PCS-MBWR part
call acalc(a,w)
tm1=+a(2)*x2 +3.0*a(3)*x4-4.0*a(9)*x5+5.0*a(11)*x6
tm2=+a(6)*x2 +2.0*a(10)*x3
tm3=-a(7)*x2 -2.0*a(12)*x3
t5 =-3.0*a(8)*x4
tm4=0.5*t5*tm0/t4*(2.0+t4*rhos*rhos)
tm4=-tm4+t5/t4
f1=rhos*tm1+0.5*tm2*rhos**2
f2=0.2*tm3*rhos**5+tm4
c . association part (based on water)
call rcalc(ri)
c . dci/dt
tm1=+ri(2)*x2 +3.0*ri(3)*x4-4.0*ri(9)*x5+5.0*ri(11)*x6
tm2=+ri(6)*x2 +2.0*ri(10)*x3
tm3=-ri(7)*x2 -2.0*ri(12)*x3
t5 =-3.0*ri(8)*x4
tmn=-2.0*ri(13)*x3
tmo=-ri(14)*x2
tmp=-ri(16)*x2
tm4=0.5*t5*tm0/t4*(2.0+t4*rhos*rhos)
tm4=-tm4+t5/t4
f3=rhos*tm1+0.5*tm2*rhos**2
f4=0.2*tm3*rhos**5+tm4
f5=1.0/3.0*rhos*rhos*rhos*tmn
f6=1.0/4.0*rhos*rhos*rhos*rhos*tmo
f7=1.0/6.0*rhos*rhos*rhos*rhos*rhos*rhos*tmp

```

```

c
  . c1
  tm1=ri(1)-ri(2)*x-ri(3)*x3+ri(9)*x4-ri(11)*x5
  tm2=ri(5)-ri(6)*x-ri(10)*x2
  tm3=ri(7)*x+ri(12)*x2+ri(15)
  t51 =ri(8)*x3
  tm4i=t51/t4 - t51*tm0/t4
  tm4i=tm4i-0.5*t51*(rhos**2)*tm0
  tmn1=ri(13)*x2
  tmo1=ri(14)*x
  tmp1=ri(16)*x
  f31=rhos*tm11+0.5*(rhos**2)*tm21
  f41=0.2*tm31*(rhos**5)+tm41
  f51=1.0/3.0*rhos*rhos*rhos*tmn1
  f61=1.0/4.0*rhos*rhos*rhos*tmo1
  f71=1.0/6.0*rhos*rhos*rhos*tm1
  . alpha2*dci/dt
  tm42=-t5*tm0*(t4*t4*rhos**4+3.0*t4*rhos*rhos+3.0)/
  &   2.0/t4/t4+3.0*t5/2.0/t4/t4
  f32=1.0/3.0*rhos*rhos*rhos*tm1+0.25*(rhos**4)*tm2
  f42=1.0/7.0*tm3*(rhos**7)+tm42
  f52=1.0/5.0*rhos*rhos*rhos*rhos*tmn
  f62=1.0/6.0*rhos*rhos*rhos*rhos*tmo
  f72=1.0/8.0*rhos*rhos*rhos*rhos*tm1
  f12=f1+f2+(ax(1)+ax(5)/x)*(f3+f4+f5+f6+f7)
  &   +ax(5)*(f31+f41+f51+f61+f71)
  &   +ax(3)*(f32+f42+f52+f62+f72)
  return
  end

```

## APPENDIX C

### DIPOLE MOMENT CORRELATION (OWENS, 1982)

```

subroutine dpm (tb,tc,xmw,vc,dpmr)
c
c .
c .   tb=normal boiling point, K
c .   tc=critical temperature, K
c .   xmw=molecular weight
c .   vc=critical volume, cc/gmole
c .   dpmr=reduced dipole moment, see equation (9)
c
c
c dimension pa(14)
c data pa/-.3378408,-2.410656,.04227894,4.568199,.09874062,
&          1.168614,-.2494797,-3.906319,-6.718836,4.173075,
&          3.735801,-.4982880,1.175132,1.100288/
c
c   tcvc=tc/vc
c   tbtc=tb/tc
c   w1=4.90147+.929177*alog(tcvc)
c   w2=7.62708*tbtc-9.84610*tbtc**2-1.23133*tbtc**3+
&      11.8132*alog(tbtc)
c   w3=30.3806+34.1873*tbtc-170.218*tbtc**2+110.755*
&      tbtc**3+18.3794*alog(tbtc)
c   ww=(w1+w2)/w3
c   hvnp=-10397.5+46.2681*tb-1373.91*tb**.5+4595.81*alog(tb)
c   p1=hvnp/xmw/100.
c   p2=vc/xmw/tc*100.
c   p3=vc/tc*xmw
c   p4=tb/tc*hvnp/xmw/1000.
c   f1=pa(1)*p1+pa(2)*p2+pa(3)*p3+pa(4)*p4
c   f2=(pa(5)*vc+pa(6)*tb+pa(7)*tc+pa(8)*hvnp/100.)/100.
c   f3=pa(9)*ww+pa(10)*ww**.5+pa(11)*alog(ww)
c   f4=pa(12)*xmw/100.+pa(13)*(xmw/100.)**2+pa(14)*alog(xmw/100.)
c   dpmr=((f1/f4+f2*f3)**2)**.5
c   return
c   end

```