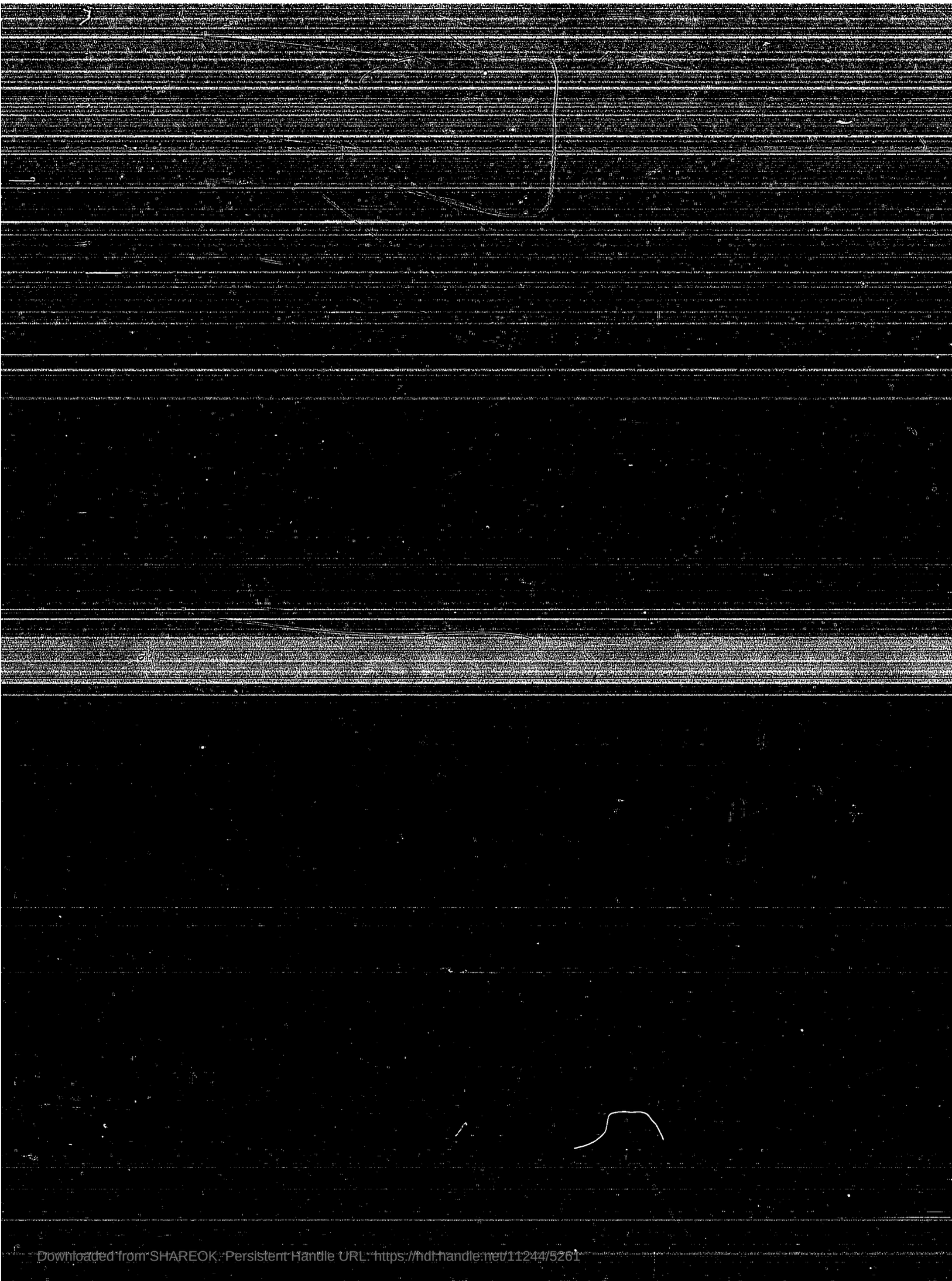


Downloaded from SHAREOK. Persistent Handle URL: https://hdl.handle.net/11244/5261

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

APPLICATION OF HYBRID MIXING RULES BASED ON THE CONFORMAL SOLUTION AND LOCAL COMPOSITION MODELS TO PREDICT THE THERMODYNAMIC PROPERTIES OF NONIDEAL SOLUTIONS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

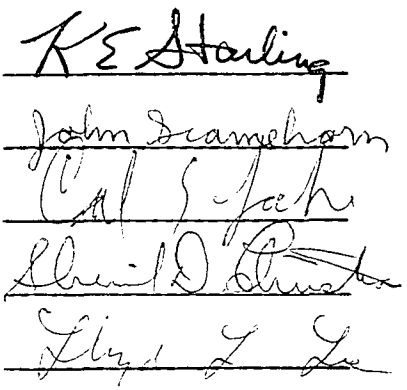
LUONG, TAI HIEP

Norman, Oklahoma

1984

APPLICATION OF HYBRID MIXING RULES BASED ON THE CONFORMAL SOLUTION AND LOCAL COMPOSITION MODELS TO PREDICT THE THERMODYNAMIC PROPERTIES OF NONIDEAL SOLUTIONS

APPROVED BY



DISSERTATION COMMITTEE

1984

LUONG, TAI HIEP

ALL RIGHTS RESERVED

ACKNOWLEDGMENTS

I would like to offer my sincere gratitude and appreciation to the following persons and organizations:

Professor K.E. Starling - for his guidance, inspiration, and encouragement throughout this research.

Professors L.L. Lee, C.E. Locke, J.F. Scamehorn, and S.D. Christian - for serving on my advisory committee.

Dr. T.H. Chung - for valuable discussions.

Dr. K.H. Kumar - for valuable advise, and encouragement.

Dr. S. Watanasiri - for valuable advise, discussions, encouragement and above all, friendship.

My parents, my sisters, and my brothers - for their love, understanding, support, and encouragement.

U.S. Department of Energy/Pittsburgh Energy Technology Center through grant # DE-FG22-80PC30249, and The Oklahoma Mining and Mineral Resources Research Institute - for financial support.

The Engineering Computer Network, and The University of Oklahoma Computing Service - for excellent computing support.

TABLE OF CONTENTS

		Page
LIST OF TABLES		vi
LIST OF ILLUSTRATIONS		viii
CHAPTER		
I.	INTRODUCTION	1
II.	EQUATION OF STATE FOR PURE FLUIDS	6
III.	REVIEW OF THE CONFORMAL SOLUTION MODEL	10
IV.	LOCAL COMPOSITION MODEL	13
V.	DEVELOPMENT OF LOCAL COMPOSITION MIXING RULES	21
	5.1 Theoretical Approach	22
	5.2 Empirical Approach	25
	5.3 Sensitivity of Composition Dependence to the Binary Interaction Parameters	28
VI.	PREDICTIONS OF THE THERMODYNAMIC PROPERTIES OF BINARY SYSTEMS	31
	6.1 Application to Nonpolar-Polar Binary Systems	34
	6.2 Application to Polar-Polar Binary Systems	59
	6.3 Application to Nonpolar-Nonpolar Binary Systems	77

Page

VII. PREDICTIONS OF THERMODYNAMIC PROPERTIES FOR MULTICOMPONENT MIXTURES 81

VIII. COMPOSITION DEPENDENCE OF THE EXCESS GIBBS FREE ENERGY 85

IX. PREDICTIONS OF LIQUID-LIQUID EQUILIBRIA 93

X. CONCLUSIONS AND RECOMMENDATIONS 102

NOMENCLATURE 105

LITERATURE CITED 108

APPENDICES

A. EXPRESSIONS FOR DERIVED THERMODYNAMIC PROPERTIES USING THE CONFORMAL SOLUTION MODEL 114

B. EXPRESSIONS FOR DERIVED THERMODYNAMIC PROPERTIES USING THE HYBRID MIXING RULES 119

C. DETAILED CALCULATIONS OF VAPOR-LIQUID EQUILIBRIA AND MIXTURE DENSITY 121

D. SOURCE LISTING OF HYBRID MIXING RULES SUBPROGRAM 127

LIST OF TABLES

TABLE		Page
II.1	Universal Constant ai and bi, to be Used in Equation (4), for the Mean-Potential-Model Four-Parameter Corresponding-States MBWR Correlation	8
VI.1	Characterization Parameters for Nonpolar Compounds for use with the Mean-Potential-Model Equation of State	32
VI.2	Characterization Parameters for Polar and Associating Compounds for use with the Mean-Potential-Model Equation of State	33
VI.3	Temperature and Pressure Ranges, and Data References for the Nonpolar-Polar Binary Systems Studied in this Work	35
VI.4	Binary Interaction Parameters for Nonpolar-Polar Binary Systems	38
VI.5	Results of Vapor-Liquid Equilibrium Predictions for Nonpolar-Polar Binary Systems	44

TABLE Page

VI.6 Temperature and Pressure Ranges, and Data References for the Polar-Polar Binary Systems Studied in this Work 64

VI.7 Binary Interaction Paramters for Polar-Polar Binary Systems 66

VI.8 Results of Vapor-Liquid Equilibrium Predictions for Polar-Polar Binary Systems 68

VI.9 Temperature and Pressure Ranges, and Data References for the Nonpolar-Nonpolar Binary Systems Studied in this Work 78

VI.10 Results of Vapor-Liquid Equilibrium Predictions, and Binary Interaction Parameters Nonpolar-Nonpolar Binary Systems 79

VII.1 Temperature and Pressure Ranges, and Data References for the Ternary Systems Studied in this Work 82

VII.2 Results of Vapor-Liquid Equilibrium Predictions for Ternary Systems 83

IX.1 Temperature and Pressure Ranges, and Data References for the Coal Fluid-Water Binary Systems Studied in this Work 94

IX.2 Binary Interaction Paramters for Coal Fluid-Water Systems (Liquid-Liquid Equilibrium) . . . 96

IX.3 Results of Liquid-Liquid Equilibrium Predictions for Coal Fluid-Water Systems 97

LISTS OF ILLUSTRATIONS

FIGURE Page

1. Local Composition Model 14
2. Plot of ε_X versus mole fractions 29
3. P-X Diagram of Ethane-Acetone at 25. C 50
4. P-X Diagram of Acetone-Cyclohexane at 25. C . . . 51
5. P-X Diagram of Cyclohexane-Aniline at 70. C . . . 53
6. P-X Diagram of Methanol-1-Methylnapthalene at 275.1 C 55
7. T-X Diagram of Methanol-n-Heptane at 1 amt . . . 56
8. P-X Diagram of n-Hexane-Ethanol at 25. C 57
9. P-X Diagram of Cyclohexane-n-Propanol at 55. C . 58
10. P-X Diagram of n-Decane-Phenol at 120. C 60
11. Saturated-Liquid Compositions in Methane-Water System 61
12. Solubility of Methane in Water at Constant Pressure 62
13. Saturated-Liquid Compositions in Ethane-Water System 63
14. P-X Diagram of CO2-Methanol at 25. C 70
15. P-X Diagram of Acetone-Water at 100. C 71

FIGURE Page

16. P-X Diagram of Acetone-Water at 150. C 72
17. P-X Diagram of Acetone-Water at 200. C 73
18. P-X Diagram of Acetone-Water at 250. C 74
19. T-X Diagram of Water-n-Butanol at 1 amt 75
20. P-X Diagram of Water-Phenol at 44.4 C 76
21. Activity Coefficients of Methanol-Benzene at 25. C 87
22. Activity Coefficients of CO2-Methanol at 25. C 88
23. Activity Coefficients of Acetone-Water at 110. C 89
24. Excess Gibbs Energy for Methanol-Benzene at 25. C 90
25. Excess Gibbs Energy for CO2-Methanol at 25. C 91
26. Excess Gibbs Energy for Acetone-Water at 100. C 92
27. Mutual Solubility of Benzene and Water 98
28. Mutual Solubility of Cyclohexane and Water . . . 99
29. Mutual Solubility of n-Hexane and Water 100
30. Mutual Solubility of Ethylbenzene and Water . . 101

ABSTRACT

Mixing rules based on the local composition and one-fluid models have been developed for use in the mean-potential-model Modified Benedict-Webb-Rubbin equation of state to accurately predict the thermodynamic properties of fluid mixtures. These hybrid mixing rules require three adjustable parameters for strongly nonideal binary mixtures and two parameters for less nonideal mixtures. These hybrid mixing rules have been tested using a wide variety of binary mixtures: (1) nonpolar+polar systems, such as hydrocarbons with ketones, alcohols, and water; (2) polar+polar systems such as carbon dioxide+ methanol, water+acetone and (3) nonpolar+nonpolar systems such as benzene+hexane, ethane+n-butane, and methane+decane. Test results show that the hybrid mixing rules can correlate vapor-liquid equilibrium and mixture density data, for these strongly nonideal solutions, better than the conformal solution model. The hybrid mixing rules with the parameters obtained from the binaries have also been applied to multicomponent mixtures.

Activity coefficients and excess Gibbs free energy were calculated using the hybrid mixing rules. Results show that reasonable predictions for these properties can be

obtained without their inclusion in the parameter determination process. The hybrid mixing rules with four adjustable parameters have been further applied to predict liquid-liquid equilibria for model coal compound+water systems. The prediction accuracy is close to the experimental uncertainty.

APPLICATION OF HYBRID MIXING RULES BASED ON THE CONFORMAL SOLUTION AND LOCAL COMPOSITION MODELS TO PREDICT THE THERMODYNAMIC PROPERTIES OF NONIDEAL SOLUTIONS

CHAPTER I

INTRODUCTION

For process design in the chemical and petroleum industries, the ability to accurately predict fluid-phase equilibria is vital for economic viability. The generalized thermodynamic correlations, with the aid of computers, have been developed to describe the behavior of the fluids over wide ranges of pressure, temperature, and composition. Although there are many correlations that can accurately predict the thermodynamic properties of pure fluids, the theoretical problem of describing the phase behavior of fluid mixtures is still largely unsolved. Predicting fluid-phase equilibria had been achieved by using either activity coefficient models or equations of state with mixing rules. For highly nonideal solutions, the activity coefficient models work well at low and moderate pressure, since they are derived from an expression for the excess Gibbs free

energy of the mixture. However, these models have several difficulties at high pressure and near the critical region where supercritical components are involved in the mixtures. With the use of equations of state, the supercritical hypothetical standard state is avoided and in addition to fluid-phase equilibria, the other thermodynamic properties can also be obtained (Reid et al., 1977).

The most frequently used theory of mixing is the van der Waals' one-fluid model or the conformal solution model (CSM) (Peng and Robinson, 1976; Starling et al., 1977). This one-fluid theory equates the thermodynamic properties of the mixture to those of a hypothetical pure fluid (at the same temperature and pressure as the mixture) whose characteristic parameters are composition dependent and often determined by semi-empirical mixing rules (Lee et al., 1979). These mixing rules are quadratic in mole fraction. The conformal solution mixing rules are briefly reviewed in chapter III. For mixtures of nonpolar and slightly polar fluids, this model gives good results (Starling et al., 1977; Peng and Robinson, 1976). However, these standard mixing rules are often not applicable to mixtures containing highly polar and associating components. The inadequacy of these simple mixing rules is due to the size and shape asymmetry and intermolecular-potential asymmetry of the molecules. The nonrandomness of molecular configurations in space arises from the asymmetry of these nonideal solutions (Whiting and Prausnitz, 1982a). To take into account

nonrandomness in liquid mixtures, the local composition concept was developed. The physical meaning of local mole fractions will be explained in chapter IV.

Based on the local composition concept, Wilson (1964) proposed an expression for the excess Gibbs free energy (or, equivalently, activity coefficient equations) which can describe the vapor-liquid equilibria (VLE) for nonideal solutions, well removed from the mixture critical region. Due to Wilson's success, several attempts have been made to apply local composition concepts to activity coefficient models for describing fluid-phase equilibria of miscible and immiscible fluids (Renon and Prausnitz, 1968; Palmer and Smith, 1972; Nitta and Katayama, 1974; Novak et al., 1974; Tsuboka and Katayama, 1975; Nagata et al., 1975; Abrams and Prausnitz, 1975). Although the local composition concept has been known for some time, it was given little attention until recently. In 1979, Huron and Vidal successfully related the activity coefficient model with a mixing rule for the energy parameter 'a' in the Redlich-Kwong (RK) equation of state. This work has demonstrated that the equation of state with mixing rules which are based on the local composition concept can be extended to strongly nonideal solutions.

The successful application of the local composition model to the mixing rules has drawn wide attention and interest. Whiting and Prausnitz (1982ab) developed density-dependent mixing rules, based on the local composition

concept, for the attractive part of the van der Waals and the Perturbed Hard Chain (PHC) equations of state. Vachhani and Anderson (1982) empirically developed a local composition density dependent mixing rule for the energy parameter of the Soave RK equation of state. Mathias and Copeman (1983) developed density dependent local composition mixing rules for the extended Peng-Robinson equation of state. These studies have shown that mixing rules based on the local composition model work better for highly nonideal solutions than the conventional one-fluid mixing rules.

Recently, at the University of Oklahoma, a mean-potential-model Modified Benedict-Webb-Rubbin (MPM-MBWR) equation of state has been developed for nonpolar, polar and associating compounds (Starling et al., 1983). This correlation can predict the thermodynamic properties of pure nonpolar, polar and associating fluids with reasonable accuracy over wide ranges of temperature and pressure. The MPM-MBWR is briefly presented in chapter II. The objective of this research is to develop mixing rules based on the local composition model, for the MPM-MBWR equation of state, to accurately predict the thermodynamic properties and phase behavior of mixtures containing nonpolar, polar and associating components. In this work the local composition concept has been used for formulating a mixing rule for the energy parameter in the MPM-MBWR equation of state. This mixing rule is a hybrid between two- and one-fluid models. The development of this mixing rule is presented in chapter

V. The hybrid mixing rules were successfully applied to predict vapor-liquid equilibria behavior for slightly and highly nonideal solutions. These highly nonideal solutions include hydrocarbon-alcohol, and hydrocarbon-water binary mixtures. The hybrid mixing rules were also extended to multicomponent mixtures. Results of these predictions are given in chapter VI and VII. In chapter VIII, the predicted excess Gibbs free energy and the activity coefficients of the binary mixtures were compared with the experimental data. The hybrid mixing rules were further tested on nearly immiscible fluids such as the mixtures of model coal compounds and water. Predictions of liquid-liquid equilibria for coal fluid-water systems are generally satisfactory. Results of these tests are given in chapter IX.

CHAPTER II

EQUATION OF STATE FOR PURE FLUIDS

The basic equation of state for pure fluids used in this work is a three-parameter corresponding-states MBWR equation (3PCS-MBWR) (Brule et al., 1982). The basic equation is:

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

where

$$T^{*} = kT/\varepsilon \tag{2}$$

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

and

$$E_i = a_i + \gamma b_i \tag{4}$$

The universal constants a_i and b_i are the isotropic and anisotropic parts, respectively, and γ is the orientation factor which accounts for the nonsphericity of the molecules. The parameters ε/k and σ^3 are the energy and size parameters. The universal constants a_i and b_i are given in table II.1.

For nonpolar and slightly polar fluids, the parameters ε/k and σ^3 were defined as:

$$\varepsilon = \varepsilon_0 = kT_c/1.2593 \tag{5}$$

and

$$\sigma^3 = 0.3189/\rho_c \tag{6}$$

For polar and associating fluids, the mean-potential-model (MPM) was utilized to account for the polar and association effects. This has been done by making the energy parameter temperature dependent (Reed and Gubbins, 1973). Hence, the energy parameter becomes:

$$\frac{\varepsilon}{k} = \frac{\varepsilon_0}{k} + \frac{\kappa}{T} \tag{7}$$

where ε_0/k is due to the nonpolar contribution, and κ is the 'lumped' parameter for polar and association contributions. The size parameter is redefined introducing an empirical parameter λ as:

$$\sigma^3 = \lambda/\rho_c \tag{8}$$

From these definitions, equations (7) and (8) will reduce to

Table II.1

Universal Constants a_i and b_i to be Used in Equation (4) for the Mean-Potential-Model Four-Parameter Corresponding-States MBWR Correlation.

i	a_i	b_i
1	1.45907	0.32872
2	6.98813	-2.64399
3	2.20704	11.3293
4	6.36121	-
5	6.59311	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

equations (5) and (6) of the original 3PCS formulation when κ is equal to zero and λ is set equal to 0.3189 for nonpolar and slightly polar compounds which have reduced dipole moments less than 0.3 (Starling et al., 1983).

The MPM correlation is an extension of the 3PCS correlation, and reguires four characterization parameters: γ, σ^3, ε/k and κ for polar and associating fluids.

CHAPTER III

REVIEW OF THE CONFORMAL SOLUTION MODEL

The one-fluid model or the so-called conformal solution model has drawn much attention from a theoretical and practical standpoint. This theory was proposed by van der Waals (VDW) (1890) nearly a century ago. Although his equation of state is out of date, his theoretical idea is still used as a guideline to develop a better model for fluid mixtures. The conformal solution formalism assumes that a mixture can be treated as a hypothetical pure pseudosubstance. The hypothetical pure pseudosubstance concept permits the equations of state developed for pure fluids to be applied to mixtures. The VDW one-fluid theory also suggests that a fluid mixture is an assembly of molecules which are randomly distributed. Strictly, the VDW one-fluid mixing rules can be applied only to mixtures of nearly equal size molecules. Consequently, prediction accuracy is lost for mixtures of differently sized molecules. Compensating for this discrepancy, the VDW one-fluid models have been modified over the years for the prediction of mixtures of molecules which differ

significantly in size and shape (Lee et al., 1979). The following general mixing rules are the extensions of rules for isotropic conformal mixtures by Smith (1972) to the anisotropic molecular solutions (Lee et al., 1979):

$$\gamma_x^k \varepsilon_x^l \sigma_x^m = \sum\sum_{ij} x_i x_j \gamma_{ij}^k \varepsilon_{ij}^l \sigma_{ij}^m \qquad (9)$$

$$\gamma_x^p \varepsilon_x^q \sigma_x^r = \sum\sum_{ij} x_i x_j \gamma_{ij}^p \varepsilon_{ij}^q \sigma_{ij}^r \qquad (10)$$

$$\gamma_x^u \varepsilon_x^v \sigma_x^w = \sum\sum_{ij} x_i x_j \gamma_{ij}^u \varepsilon_{ij}^v \sigma_{ij}^w \qquad (11)$$

The exponents k, l, m, p, q, r, u, v, w in equations (9), (10) and (11) can be determined theoretically or empirically. In order to improve the predictions for mixtures of large molecular dissimilarities, Lee et al., (1979) determined these exponents empirically by fitting vapor-liquid equilibrium data. The optimal values of the exponents are k=0, l=0, m=4.5, p=0, q=1, r=4.5, u=1, v=0 and w=3.5. Hence, the final formulation of the semiempirical mixing rules is:

$$\sigma_x^{4.5} = \sum\sum_{ij} x_i x_j \sigma_{ij}^{4.5} \qquad (12)$$

$$\varepsilon_x \sigma_x^{4.5} = \sum\sum_{ij} x_i x_j \varepsilon_{ij} \sigma_{ij}^{4.5} \qquad (13)$$

$$\gamma_x \sigma_x^{3.5} = \sum\sum_{ij} x_i x_j \gamma_{ij} \sigma_{ij}^{3.5} \qquad (14)$$

With the combining rules:

$$\sigma_{ij} = \xi_{ij} (\sigma_i \sigma_j)^{\frac{1}{2}} \tag{15}$$

$$\varepsilon_{ij} = \zeta_{ij} (\varepsilon_i \varepsilon_j)^{\frac{1}{2}} \tag{16}$$

and

$$\gamma_{ij} = \frac{1}{2} (\gamma_i + \gamma_j) \tag{17}$$

where ξ_{ij} and ζ_{ij} are binary interaction parameters. The component energy parameters ε_i and ε_j are determined from equation (7)

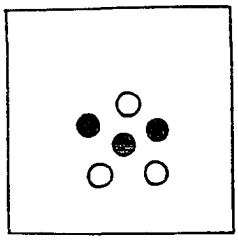
Expressions for enthalpy departure, entropy departure, fugacity coefficient and other properties can be derived from the compressibility factor expression via the classical thermodynamic relations (Reid et al., 1977). The derived thermodynamic properties expressions for conformal mixtures are given in appendix A.

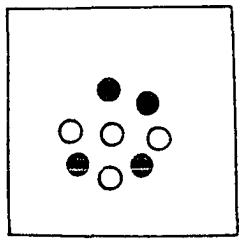
These semiempirical mixing rules with the MPM correlation have been successfully applied to nonpolar and slightly polar mixtures, but they fail badly for mixtures containing highly polar and/or associating components such as water, alcohols , etc...

CHAPTER IV

LOCAL COMPOSITION MODEL

In a real fluid mixture, the motions, positions and orientations of the molecules are strongly affected by their neighboring molecules due to asymmetry in a complex mixture. The complexity of the mixtures may arise from size and shape asymmetry and intermolecular-potential asymmetry. For a mixture containing several types of molecules having significant differences in interaction energies, there are some molecule types which prefer to cluster around one particular molecule type rather than another. This causes an unequal spatial distribution of molecules of a given type in the mixture, in contrast to the conventional assumption that the molecules are randomly distributed. The nonrandomness of the molecular configurations in space is assumed due to the preferential interactions between different kinds of molecules in the mixture. These intermolecular forces will cause the local mole fractions to differ from the bulk mole fractions. For a simple visualization of the physical meaning of local compositions, the following example is given (see Figure 1.). For a binary system, according to the





Molecule A ● at center — Molecule B ○ at center

A-cell — B-cell

An equimolar mixture of A and B molecules

Cell Type :	A	B
Interaction energies :	E_{AA} and E_{BA}	E_{BB} and E_{AB}
Number of molecules around central molecule :		
A-molecules	n_{AA} : 2	n_{AB} : 4
B-molecules	n_{BA} : 3	n_{BB} : 3
Total :	5	7

Local compositions :

x_{AA} = 2/5 = 0.40

x_{BA} = 3/5 = 0.60

x_{BB} = 3/7 = 0.43

x_{AB} = 4/7 = 0.57

Overall Compositions :

x_A = 7/14 = 0.5

x_B = 7/14 = 0.5

Figure 1. Local Composition Model

two-fluid theory of Scott (1956), there are two types of cells: the A-cell which has a molecule of type A at the center with nearest neighbors of components A and B, and the B-cell which has a molecule of type B at the center, again with nearest neighbors of components A and B. The local mole fractions may be defined as:

$$x_{AA} = \frac{n_{AA}(L_{AA})}{n_{AA}(L_{AA}) + n_{BA}(L_{BA})} \tag{18}$$

$$x_{BA} = \frac{n_{BA}(L_{BA})}{n_{AA}(L_{AA}) + n_{BA}(L_{BA})} \tag{19}$$

$$x_{BB} = \frac{n_{BB}(L_{BB})}{n_{BB}(L_{BB}) + n_{AB}(L_{AB})} \tag{20}$$

and

$$x_{AB} = \frac{n_{AB}(L_{AB})}{n_{BB}(L_{BB}) + n_{AB}(L_{AB})} \tag{21}$$

where n_{ji} is the number of molecules of type j around a central molecule of type i within a spherical volume of radius L_{ji}, and x_{ji} is the local mole fraction of component j molecules surrounding a central molecule of type i. The

local compositions deviate from the overall compositions due to the strength of the A-B interactions relative to the A-A and B-B interactions (see Figure1).

The local composition concept was originated from Guggenheim (1935, 1952, 1966). This concept was applied to regular solutions and considered only the first neighbor region in the lattice gas. Although the local composition model has been studied extensively using molecular dynamic calculations and Monte Carlo calculations (Nakanashi and Toukubo, 1979; Nakanishi et al., 1982; Panayiotou and Vera, 1981; Kemeny and Rasmussen 1981; Fischer and Lago, 1983; Lee et al., 1983; Hu and Prausnitz, 1983; Hoheisel et al., 1983), it is still a controversial theory. The most successful investigation of the theoretical foundations of the local composition model was obtained recently by Lee et al., (1983) by using statistical mechanics. Their statistical mechanical local composition theory not only yields a better understanding of the local composition model, but also shed light on the least-understood theoretical problem of liquid mixtures. From the statistical mechanical standpoint, Lee et al. (1983) defined the n_{ji} in a binary system as:

$$n_{AA}(L_{AA}) \equiv \rho_A \int_0^{L_{AA}} dr \; 4\pi r^2 \, g_{AA}(r) \qquad (22)$$

$$n_{BA}(L_{BA}) \equiv \rho_B \int_0^{L_{BA}} dr \; 4\pi r^2 \, g_{BA}(r) \tag{23}$$

$$n_{BB}(L_{BB}) \equiv \rho_B \int_0^{L_{BB}} dr \; 4\pi r^2 \, g_{BB}(r) \tag{24}$$

and

$$n_{AB}(L_{AB}) \equiv \rho_A \int_0^{L_{AB}} dr \; 4\pi r^2 \, g_{AB}(r) \tag{25}$$

where $g_{ij}(r)$ are the radial distribution functions for the fluid. Substitute the equations above into equations (18), (19), (20), and (21), the local mole fractions can be expressed in term of the radial distribution functions:

$$x_{AA} = \frac{\rho_A \int_0^{L_{AA}} dr \; 4\pi r^2 g_{AA}(r)}{\rho_A \int_0^{L_{AA}} dr \; 4\pi r^2 g_{AA}(r) + \rho_B \int_0^{L_{BA}} dr \; 4\pi r^2 g_{BA}(r)} = \frac{n_{AA}}{z_A} \tag{26}$$

$$x_{BA} = \frac{\rho_B \int_0^{L_{BA}} dr \; 4\pi r^2 g_{BA}(r)}{\rho_A \int_0^{L_{AA}} dr \; 4\pi r^2 g_{AA}(r) + \rho_B \int_0^{L_{BA}} dr \; 4\pi r^2 g_{BA}(r)} = \frac{n_{BA}}{z_A} \tag{27}$$

$$x_{BB} = \frac{\rho_B \int_0^{L_{BB}} dr\ 4\pi r^2 g_{BB}(r)}{\rho_B \int_0^{L_{BB}} dr\ 4\pi r^2 g_{BB}(r) + \rho_B \int_0^{L_{AB}} dr\ 4\pi r^2 g_{AB}(r)} = \frac{n_{BB}}{z_B} \quad (28)$$

and

$$x_{AB} = \frac{\rho_A \int_0^{L_{AB}} dr\ 4\pi r^2 g_{AB}(r)}{\rho_B \int_0^{L_{BB}} dr\ 4\pi r^2 g_{BB}(r) + \rho_A \int_0^{L_{AB}} dr\ 4\pi r^2 g_{AB}(r)} = \frac{n_{AB}}{z_B} \quad (29)$$

or

$$x_{AA} = \frac{x_A}{x_A + x_B \Lambda_{BA}} \quad (30)$$

$$x_{BA} = \frac{x_B \Lambda_{BA}}{x_A + x_B \Lambda_{BA}} \quad (31)$$

$$x_{BB} = \frac{x_B}{x_B + x_A \Lambda_{AB}} \quad (32)$$

and

$$x_{AB} = \frac{x_A \Lambda_{AB}}{x_B + x_A \Lambda_{AB}} \tag{33}$$

where

$$\Lambda_{BA} = \frac{\int_0^{L_{BA}} dr\, 4\pi r^2 g_{BA}(r)}{\int_0^{L_{AA}} dr\, 4\pi r^2 g_{AA}(r)} \tag{34}$$

and

$$\Lambda_{AB} = \frac{\int_0^{L_{AB}} dr\, 4\pi r^2 g_{AB}(r)}{\int_0^{L_{BB}} dr\, 4\pi r^2 g_{BB}(r)} \tag{35}$$

and z_i is the coordination number. From the above definitions, second and third neighbors have been ignored in the expressions of the local compositions. Λ_{BA} and Λ_{AB} can further be defined as:

$$\Lambda_{BA} = \frac{V_{BA} \exp(-\beta W_{BA})}{V_{AA} \exp(-\beta W_{AA})} \tag{36}$$

and

$$\Lambda_{AB} = \frac{V_{AB} \exp(-\beta W_{AB})}{V_{BB} \exp(-\beta W_{BB})} \tag{37}$$

where V_{ij} is the spherical volume, $(4/3\ \pi)L_{ij}^3$, and W_{ij} is the mean potential of mean force of Kirkwood (1935). If the radii are chosen to be equal, $L_{AA} = L_{BA} = L_{BB} = L_{AB}$, the ratio V_{BA}/V_{AA} and V_{AB}/V_{BB} would be unity. The conservation equations in both cells are:

$$x_{BA} + x_{AA} = 1 \tag{38}$$

and

$$x_{AB} + x_{BB} = 1 \tag{39}$$

with the above equations the local composition equations can be rewritten as:

$$\frac{x_{BA}}{x_{AA}} = \frac{x_B}{x_A} \frac{\exp(-W_{BA}/RT)}{\exp(-W_{AA}/RT)} \tag{40}$$

and

$$\frac{x_{AB}}{x_{BB}} = \frac{x_A}{x_B} \frac{\exp(-W_{AB}/RT)}{\exp(-W_{BB}/RT)} \tag{41}$$

According to the above definitions, the local compositions are proportional to the overall compositions, weighted by Boltzmann factors whose arguments characterize the like and unlike two-body interactions.

CHAPTER V

DEVELOPMENT OF LOCAL COMPOSITION MIXING RULES

Accurate equation of state mixing rules for prediction of thermodynamic properties for a wide range of fluid mixtures have not yet been developed in spite of their importance in engineering and industry. Several mixing rules work well for simple fluid mixtures, but are less successful for complex mixtures. The main problem in the development arises from the liquid phase, which is neither completely random nor totally structured. To account for strongly nonideal solutions, the local compositions have been used for modeling the liquid phase activity coefficients. In calculating vapor-liquid equilibria, the activity coefficient models were applied only in the liquid phase where most of the nonidealities occur while the equation of state is used for the vapor phase which is less nonideal. The local composition model gives an effective treatment of the liquid structure. It contains information concerning the nonidealities and the unusual interactions of the molecules in a mixture. Consequently, the local composition model gives satisfactory results. Due to the successful

application of the local compositions for the activity coefficients, the local compositions have been used for modeling the equation of state mixing rules in recent years.

This chapter shows the development of local composition mixing rules for the MPM correlation from theoretical and empirical approaches. In this work, an empirical approach was used to develop mixing rules for the MPM correlation for practical reasons.

5.1 Theoretical Approach

Whiting and Prausnitz (1983a,b) treated the interaction energy W_{ij} in equations (40) and (41) as that is, the Helmholtz free energy. This was later verified by Lee et al., (1983), W_{ij} is defined from the Helmholtz free energy. Therefore, W_{ij} depends on density and temperature. Unlike Whiting and Prausnitz, who related W_{ij} to the attractive part of the Helmholtz free energy, both the attractive and the repulsive contributions to the Helmholtz free energy are included in the evaluation of W_{ij} in this study. Consequently, the interaction energy W_{ij} can be determined from any equation of state, regardless of whether or not the equation of state can be separated into repulsive and attractive parts. Nevertheless, the method used for developing mixing rule in this section is in the spirit of that used by Whiting and Prausnitz. Assuming pairwise additive interactions, the total molar configurational

internal energy is:

$$\frac{U}{N} = x_1(x_{21}\, u_{21} + x_{11}\, u_{11}) + x_2(x_{12}\, u_{12} + x_{22}\, u_{22}) \tag{42}$$

where u_{ij} is the molar internal energy of the two body interaction between molecules of type i and j. From the classical thermodynamic relations, the Helmholtz free energy can be obtained from:

$$U = \left.\frac{\partial\,(A/T)}{\partial\,(1/T)}\right|_{N,V} \tag{43}$$

By combining equations (40) through (43) and using $H_{ij} = \alpha A_{ij}$, the total internal energy can be expressed as:

$$U = \frac{-\sum_{i=1}^{2} x_i \sum_{j=1}^{2} x_j \left[\left.\frac{\partial\,(A_{ij}/T)}{\partial\,(1/T)}\right|_{N,V}\right] \exp(-\alpha A_{ij}/RT)}{\sum_{j=1}^{2} x_j \exp(-\alpha A_{ij}/RT)} \tag{44}$$

where α is defined as 2/z. From the Gibbs-Helmholtz relation, equation (43), the molar Helmholtz can be determined by:

$$A = T\int_0^{1/T} d(1/T)\; U$$

$$= \frac{-RT}{\alpha} \sum_{i=1}^{2} x_i \ln \sum_{j=1}^{2} F_{ij} x_j \exp(-\alpha A_{ij}/RT) \qquad (45)$$

where, following Whiting and Prausnitz, F_{ij} arises from the lower limit of the intergration at infinite temperature. For mixtures of equal sized molecules, $F_{ij} = 1$ is a reasonable assumption. Equation (45) can be rewritten as:

$$\frac{A}{RT} = \sum_{i=1}^{2} x_i \frac{A_i}{RT} - \frac{1}{\alpha} \sum_{i=1}^{2} x_i \ln \sum_{j=1}^{2} x_j F_{ij} \exp(-\alpha (A_{ij} - A_{ii})/RT) \qquad (46)$$

The expression for the pressure P can be obtained by differentiating equation (46) with respect to specific volume v:

$$P = \sum_{i=1}^{2} x_i P_i - \frac{\sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \left[\frac{\partial (A_{ij} - A_{ii})}{\partial v} \bigg|_{T,x} \right] \exp(-\alpha_{ij} (A_{ij} - A_{ii})/RT)}{\sum_{j=1}^{2} x_j \exp(-\alpha_{ij} (A_{ij} - A_{ii})/RT} \qquad (47)$$

where P_i is determined at the temperature and density of the mixture. For pure fluid predictions, the second term vanishes and the first term becomes the pure fluid equation of state. These density-dependent local composition mixing

rules were applied to predict vapor-liquid equilibria for several nonideal mixtures of similar size molecules (Luong, et al., 1983). The results were better than those obtained by the conventional conformal solution mixing rules. For mixtures of widely different sized molecules, these mixing rules encountered difficulties. The problems arise from the liquid density search, consequently it prohibits vapor-liquid equilibria calculations. Therefore, these density-dependent local composition mixing rules are not applicable. The next section shows an empirical approach to apply the spirit of local compositions to the mixing rules for the MPM correlation.

5.2 Empirical Approach

This section shows a different method for extending the MPM correlation to mixtures. The local composition model was used for modeling the mixing rule for the characteristic energy parameter ε_X. By analogy to the total configurational internal energy in equation (42) the characteristic energy parameter ε_X of the mixture can be defined as:

$$\varepsilon_X = x_1(x_{21}\,\varepsilon_{21} + x_{11}\,\varepsilon_{11}) + x_2(x_{12}\,\varepsilon_{12} + x_{22}\,\varepsilon_{22}) \qquad (48)$$

where ε_{ij} is the characteristic energy of the two body interaction between i and j molecules. Substituting the

local composition equations (38), (39), (40) and (41) into equation (48), the expression for the energy parameter ε_x for a binary system is:

$$\varepsilon_x = \frac{x_1^2 \varepsilon_{11}}{x_1 + x_2 e^{(-\Delta_{12}/RT)}} + \frac{x_1 x_2 \varepsilon_{12} e^{(-\Delta_{12}/RT)}}{x_1 + x_2 e^{(-\Delta_{12}/RT)}}$$

$$+ \frac{x_1 x_2 \varepsilon_{21} e^{(-\Delta_{21}/RT)}}{x_2 + x_1 e^{(-\Delta_{21}/RT)}} + \frac{x_2^2 \varepsilon_{22}}{x_2 + x_1 e^{(-\Delta_{21}/RT)}} \qquad (49)$$

where

$$\Delta_{12} = W_{12} - W_{11} \qquad (50)$$

$$\Delta_{21} = W_{21} - W_{22} \qquad (51)$$

For multicomponent mixtures, equation (49) can be expressed as:

$$\varepsilon_x = \Sigma\, x_i \frac{\Sigma\, x_j\, \varepsilon_{ij} \exp(-\Delta_{ij}/RT)}{\Sigma\, x_k \exp(-\Delta_{ik}/RT)} \qquad (52)$$

The mixing rule above for the energy parameter ε_x introduces two more adjustable parameters $\Delta_{12}=(W_{12}-W_{11})$ and $\Delta_{21}=(W_{21}-W_{22})$, in addition to a binary parameter ζ_{ij} which arises from the combining rule for ε_{ij} in equation (16). This mixing rule can be reduced to the classical conformal solution mixing rule by a straightforward choice of parameters in which both Δ_{12} and Δ_{21} are set equal to 0.

The following conventional conformal solution mixing rules for σ_x^3 and γ_x were used in this work:

$$\sigma_x^3 = \Sigma \Sigma x_i x_j \sigma_{ij}^3 \qquad (53)$$

and

$$\gamma_x \sigma_x^3 = \Sigma \Sigma x_i x_j \gamma_{ij} \sigma_{ij}^3 \qquad (54)$$

Equations (53) and (54) correspond to the use of the following values of exponents in equations (9) and (11), k=0, l=0, n=3, u=1, v=0 and w=3. These exponents were determined empirically using vapor-liquid equilibrium data. The combining rule equations (15) and (17) are also applicable to σ_{ij} and γ_{ij}.

The hybrid mixing rules above for ε_x, σ_x^3 and γ_x, equations (52), (53) and (54), were used for the HPM correlation in this study. Three binary parameters ζ_{ij}, Δ_{12}

and Δ_{21} were required for strongly nonideal solutions (e.g., solutions of alcohols and hydrocarbons). For moderately nonideal mixtures (e.g., nonpolar mixtures), two binary parameters ξ_{ij} and ζ_{ij} were required, while Δ_{12} and Δ_{21} were set equal to 0. These binary parameters were determined from vapor-liquid equilibrium data for the binary systems. Although the mixing rule for ε_x is based on the local composition model, it still lies within the one-fluid model because ε_x is related to ε of the pure components by a set of mixing rules. Only the spirit of the local composition model is retained.

The derived thermodynamic properties relations for mixtures are given in appendix B.

5.3 Sensitivity of Composition Dependence to the Binary Parameters

The mixing rule, equation (52), requires three parameters ζ_{ij}, Δ_{12} and Δ_{21} to define the characteristic energy parameter ε_x. The two additional binary parameters Δ_{12} and Δ_{21} provide flexibility to this mixing rule. Figure 2 shows the composition dependence of the energy parameter ε_x for a binary system. Differences in values of Δ_{12} and Δ_{21} produce a variety of curves (e.g., the s shape curve). When Δ_{12} and Δ_{21} are set equal to 0, this mixing rule reduces to the quadratic mixing rule. Consequently, this mixing rule contains, as an optional possibility, the conventional

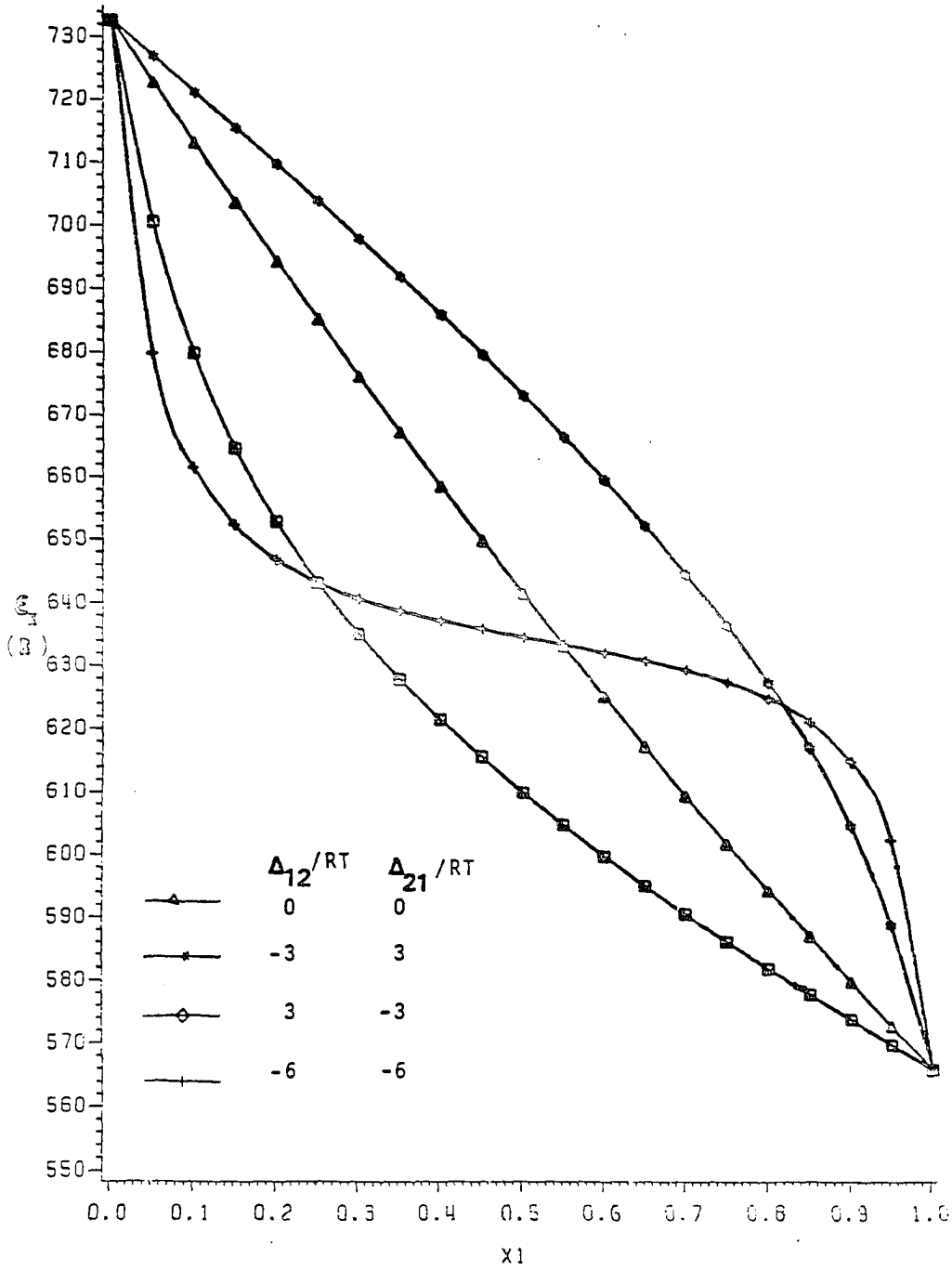


Figure 2: ξ_1 versus X_1

mixing rule. Furthermore, at high temperature the exponent terms in this mixing rule approach unity, and the classical rule is again obtained. As a result, these two binary parameters give the energy parameter ε_x a wide range of variations and possibly applicability to highly nonideal solutions.

CHAPTER VI

PREDICTIONS OF THERMODYNAMIC PROPERTIES OF BINARY SYSTEMS

The hybrid mixing rules (HMR) with the mean-potential-model correlation were used to correlate the thermodynamic properties of several representative binary systems. These systems were categorized by their polarities such as nonpolar+polar, polar+polar and nonpolar+nonpolar binary mixtures. The vapor-liquid equilibria calculations were performed both at low and elevated pressure. The pure characterization parameters for used with the MPM correlation are given in table VI.1 and VI.2. To provide further perspective on the accuracy achieved by the hybrid mixing rules, the conformal solution model (CSM) with two binary parameters were also used in this research. The mixing rules developed in this work required two to three parameters for highly nonideal solutions. In this work the adjustable parameters were determined from VLE data. The regression technique developed by Britt-Luecke (1973) was used in the determination of the parameters for most of the binary systems with the exception of several binary mixtures wherein the regression method of Goin (1978) was used. The

Table VI.1

Characterization Parameters for Nonpolar Compounds for use with the Mean-Potential-Model Equation of Sate

Compound	Mw	ϵ_o/k*1.2593 (K)	σ^3/0.3189 (cc/gmole)	γ	$\epsilon/1000$ (K^2)
Hydrogen	2.016	32.95	64.14	0.00	0.0
Methane	16.042	190.69	99.50	0.01289	0.0
Ethane	30.07	305.40	148.0	0.09623	0.0
Propane	44.097	369.79	203.0	0.1538	0.0
n-Butane	58.12	425.7	255.0	0.1991	0.0
Benzene	78.115	562.09	257.97	0.218	0.0
Cyclohexane	84.163	553.00	307.53	0.2159	0.0
n-Hexane	86.178	507.39	370.00	0.3054	0.0
Toluene	92.142	591.72	315.29	0.2665	0.0
Methylcyclohexane	98.189	572.09	368.0	0.233	0.0
n-Heptane	100.21	540.29	426.13	0.3499	0.0
Ethylbenzene	106.168	617.09	374.0	0.301	0.0
Ethylcyclohexane	112.21	608.09	450.0	0.243	0.0
Tetralin	132.207	720.0	439.63	0.3232	0.0
n-Decane	142.276	617.56	602.01	0.4880	0.0
1-Methylnapthalene	142.20	771.98	445.91	0.3538	0.0
1-Ethylnapthalene	156.226	775.59	4480.7	0.3538	0.0
n-Hexadecane	226.43	717.22	975.44	0.7122	0.0

* The quantities in the parenthese are the units of the parameters.

Table VI.2

Characterization Parameters for Polar and Associating Compounds for use with the Mean-Potential-Model Equation of Sate

Compound	Mw	ϵ_o/k (K)	σ^3 (cc/gmole)	γ	K/1000 (K^2)
Water	18.015	547.40	16.900	0.3453	-11.123
Hydrogen Sulfide	34.076	291.12	30.105	0.0840	1.806
Carbon Dioxide	44.01	241.02	28.98	0.220	0.4153
Methanol	32.042	414.6	38.24	0.4218	2.781
Ethanol	46.069	388.9	52.12	0.4152	13.494
Propanol	60.096	413.5	67.79	0.5299	7.602
n-Butanol	74.123	419.8	86.91	0.6608	6.929
Phenol	94.113	509.3	86.54	0.2883	27.112
Diethyl Ether	74.123	373.9	89.01	0.281	-0.780
Acetone	58.08	407.3	68.82	0.3000	0.5268
2-Butanone	72.107	440.8	81.92	0.365	-6.057
Tetrahydrofuran	72.107	429.1	73.47	0.2144	0.916
Aniline	93.129	541.0	89.79	0.2779	14.198
Pyridine	79.102	4993.7	75.95	0.237	0.705

algorithm for calculating VLE used in this work was described by Boston and Britt (1978).

6.1 Application to Nonpolar-Polar Binary Systems

The hybrid mixing rules (HMR) were tested using vapor-liquid equilibrium data for twenty-four nonpolar+polar binary mixtures. These binary systems are hydrocarbons with ketones, aniline, alcohols, phenol and water. Each binary system, the names of the components, the temperature and pressure ranges of the data, and the references from which the data were taken are listed in table VI.3. The binary parameters determined from regression analysis of the VLE data are reported in table VI.4. Results of the fit are presented in table VI.5 in terms of percent average absolute relative deviations (% AARD). In general, the HMR gives better results than the CSM. Figure 3 shows the experimental and the calculated pressure-composition diagram for ethane-acetone system at 25 C. The solid lines represent the results from the HMR and the dashed lines are predicted from the CSM. The HMR yields better agreement between experimental and calculated values than the CSM. Although both types of mixing rules predicted accurately the vapor phase compositions, the HMR greatly improved liquid phase composition predictions. Figure 4 shows results for acetone-cyclohexane mixture which exhibits azeotrope. The HMR correctly and accurately predicted the azeotrope.

Table VI.3

Temperature and Pressure Ranges, and Data References for the Nonpolar - Polar Binary Systems Studied in This Work.

Systems (1) -- (2)	Pro.	No. of points	T range K	P range atm	Data References
Hydrocarbons and Ketones					
Ethane-Acetone	VLE	8	298	4-39	Ohgaki et al. 1976
Acetone-Cyclohexane	VLE	23	298	0.15-0.32	Tasic et al. 1978
Cyclohexane-2-Butanone	VLE	10	348-350	1	Donald et al. 1956
	ρ	9	298	1	Donald et al. 1956
Hydrocarbons and Aniline					
Benzene-Aniline	VLE	22	343-363	0.23-0.68	Hosseini et al. 1963
Cyclohexane-Aniline	VLE	18	343-363	0.32-0.67	Hosseini et al. 1963
Toluene-Aniline	VLE	40	353-373	0.09-0.67	Schneider 1960
Methylcyclohexane-Aniline	VLE	43	353-373	0.24-0.92	Schneider 1960

Table VI.3 (Continued)

Systems (1) -- (2)	Pro.	No. of points	T range K	P range atm	Data References
Hydrocarbons and Alcohols					
Methanol-Benzene	VLE	9	298	0.21-0.24	Hwang et al. 1977
	VLE	18	308-328	0.26-0.89	Scatchard et al. 1946
	ρ	35	293-313	1	Sumer et al. 1967
					Scatchard et al. 1946
Methanol-Toluene	VLE	10	336-344	1	Benedict et al. 1945
		27	293-313	1	Sumer et al. 1967
Methanol-n-Heptane	VLE	9	331-334	1	Benedict et al. 1945
Methanol-1-Methylnapthalene	VLE	48	521-573	12.9-119.0	Paulaitis 1983
Benzene-Ethanol	VLE	9	298	0.11-0.16	Smith et al. 1970
	VLE	9	328	0.47-0.62	Yuan et al. 1963
Ethanol-Cyclohexane	VLE	9	298	0.14-0.18	Hwang et al. 1977
	VLE	7	328	0.44-0.55	Scatchard et al. 1964
n-Hexane-Ethanol	VLE	9	298	0.19-0.25	Smith et al. 1970
	VLE	18	318-328	0.45-0.88	Kudryavtseva et al. 1963
Ethanol-Toluene	VLE	9	328	0.26-0.32	Gmehling et al. 1977 b
	ρ	12	298	1	Kretschmer et al. 1949

Table VI.3 (Continued)

Systems (1) -- (2)	Pro.	No. of points	T range K	P range atm	Data References
Benzene-n-Propanol	VLE	9	298	0.07-0.12	Hwang et al. 1977
	VLE	13	318	0.11-0.31	Gmehling et al. 1977 b
Cyclohexane-n-Propanol	VLE	9	298	0.14-0.18	Hwang et al. 1977
	VLE	17	328	0.18-0.5	Strubl et al. 1970
n-Propanol-n-Heptane	VLE	9	357-363	0.60-0.76	Gurukul et al. 1966
	ρ	9	303	1	Gurukul et al. 1966
Benzene-n-Butanol	VLE	46	298-403	0.06-2.90	Gmehling et al. 1977 c
Toluene-n-Butanol	VLE	25	363-372	0.37-0.84	Gmehling et al. 1977 c
		Hydrocarbons and Phenol			
Benzene-Phenol	VLE	28	353	0.23-0.97	Gmehling 1982
	VLE	12	343	0.31-0.69	Martin et al. 1933
n-Decane-Phenol	VLE	15	393	0.20-0.26	Gmehling 1982
		Hydrocarbons and Water			
Methane-Water	VLE	90	373-613	200-10000	Olds et al. 1942 Culberson et al. 1951
Ethane-Water	VLE	76	433-613	200-10000	Reamer et al. 1943 Culberson et al. 1950

1 VLE = Vapor-Liquid equilibrium, ρ = density, Pro. = Property

Table VI.4

Binary Interaction Parameters for Nonpolar-Polar Binary Systems

Systems (1) - (2)	Model*	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
			Hydrocarbons and Ketones			
Ethane-Acetone	H.M.R.		1.0000	0.9134	-302.25	1166.42
	C.S.M.		0.9858	0.9404	-	-
Acetone-Cyclohexane	H.M.R.		1.0000	0.9737	-1350.14	-483.50
	C.S.M.		1.0980	0.9016	-	-
Cyclohexane-2-Butanone	H.M.R.		1.0000	0.9607	-1104.30	-383.96
	C.S.M.		0.6182	1.1523	-	-
			Hydrocarbons and Aniline			
Cyclohexane-Aniline	H.M.R.		1.0000	0.9231	-544.49	633.45
	C.S.M.		0.9712	0.9754	-	-
Toluene-Aniline	H.M.R.		1.0000	1.0000	553.49	-308.73
	C.S.M.		0.9939	0.9933	-	-

Table VI.4 (Continued)

Systems (1) - (2)	Model*	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
Benzene-Aniline	H.M.R.		1.0000	1.0000	110.70	119.61
	C.S.M.		0.9919	0.9937	-	-
Methylcyclohexane-Aniline	H.M.R.		1.0000	0.9384	-249.95	223.18
	C.S.M.		0.9786	0.9801	-	-
Hydrocarbons and Alcohols						
Methanol-Benzene	H.M.R.	298.15	1.0000	0.9536	-1186.75	-1164.57
	C.S.M.		0.7675	0.9492	-	-
	H.M.R.	309.15	1.0000	0.9507	-963.37	-1087.91
	C.S.M.		0.7004	0.9592	-	-
	H.M.R.	328.15	1.0000	0.9416	-294.12	-1012.22
	C.S.M.		0.7147	0.9686	-	-
Methanol-n-Heptane	H.M.R.		1.0000	0.9166	-881.60	-879.53
	C.S.M.		0.7304	0.9551	-	-
Methanol-Toluene	H.M.R.		1.0000	0.9175	1627.55	-372.31
	C.S.M.		1.2549	0.8835	-	-

Table VI.4 (Continued)

Systems (1) - (2)	Model*	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
Methanol-1-Methyl napthalene	H.M.R.		0.9047	1.0000	1559.32	54.88
	C.S.M.		1.0611	0.7626	-	-
n-Hexane-Ethanol	H.M.R.	298.15	1.0000	0.9356	-2197.44	99.34
	C.S.M.		0.8775	0.9838	-	-
	H.M.R.	318.15	1.0000	0.9299	-1925.47	39.44
	C.S.M.		0.8331	0.9787	-	-
	H.M.R.	328.15	1.0000	0.9255	-1496.88	30.96
	C.S.M.		0.8407	0.9684	-	-
Ethanol-Cyclohexane	H.M.R.	298.15	1.0000	0.9481	-497.27	-1308.67
	C.S.M.		0.6599	1.0136	-	-
	H.M.R.	323.15	1.0000	0.9492	-577.73	-1363.08
	C.S.M.		0.4180	1.6357	-	-
Benzene-Ethanol	H.M.R.	298.15	1.0000	0.9563	-1213.06	-196.31
	C.S.M.		0.7569	0.9715	-	-
	H.M.R.	328.15	1.0000	0.9406	-820.77	808.63
	C.S.M.		0.6096	1.0635	-	-
Ethanol-Toluene	H.M.R.		1.0000	0.9440	-608.93	-398.79
	C.S.M.		1.2650	0.9004	-	-

Table VI.4 (Continued)

Systems (1) - (2)	Model*	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
Benzene-n-Propanol	H.M.R.	298.15	1.0000	0.9643	-1175.17	-484.59
	C.S.M.		0.9272	0.9580	-	-
	H.M.R.	318.15	1.0000	0.9607	-1401.61	120.28
	C.S.M.		0.8582	0.9654	-	-
Cyclohexane-n-Propanol	H.M.R.	298.15	1.0000	0.9578	-1492.14	-31.49
	C.S.M.		0.8925	0.9604	-	-
	H.M.R.	328.15	1.0000	0.9566	-1995.14	-241.86
	C.S.M.		0.8538	0.9614	-	-
n-Propanol-n-Heptane	H.M.R.		1.0000	0.9424	-578.31	-1128.33
	C.S.M.		0.7341	1.0054	-	-
Toluene-n-Butanol	H.M.R.	363.15	1.0000	0.9543	-779.28	-40.32
	C.S.M.		0.7699	0.9832	-	-
	H.M.R.	373.15	1.0000	0.9591	-831.36	-803.92
	C.S.M.		0.7642	0.9978	-	-
Benzene-n-Butanol	H.M.R.		1.0000	0.9412	-824.84	-2367.68
	C.S.M.		0.9372	0.9597	-	-

Table VI.4 (Continued)

Systems (1) - (2)	Model*	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
			Hydrocarbons and Phenol			
Benzene-Phenol	H.M.R.		1.0000	0.9082	-1884.00	1861.19
	C.S.M.		0.9896	0.9912	-	-
n-Decane-Phenol	H.M.R.		1.0000	0.9101	3319.93	-628.90
	C.S.M.		0.9476	0.9493	-	-
			Hydrocarbons and Water			
Methane-Water	H.M.R.	310.92	1.0000	0.7513	3040.41	3431.63
	C.S.M.		0.8205	0.9269	-	-
	H.M.R.	344.26	1.0000	0.7493	3188.80	2399.24
	C.S.M.		0.8324	0.9351	-	-
	H.M.R.	377.60	1.0000	0.7304	3682.69	2083.65
	C.S.M.		0.8320	0.8900	-	-
	H.M.R.	410.93	1.0000	0.6932	4401.27	2034.53
	C.S.M.		0.8507	0.9450	-	-
	H.M.R.	444.26	1.0000	0.6643	5202.46	2014.98
	C.S.M.		0.8573	0.9550	-	-

Table VI.4 (Continued)

Systems (1) - (2)	Model*	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
Ethane-Water	H.M.R.	344.26	1.0000	0.6227	1716.94	1488.96
	C.S.M.		0.7196	0.3885	-	-
	H.M.R.	373.60	1.0000	0.6078	1868.42	1290.58
	C.S.M.		0.7323	0.4180	-	-
	H.M.R.	410.93	1.0000	0.6000	2056.75	1105.56
	C.S.M.		0.7843	0.6694	-	-
	H.M.R.	444.26	1.0000	0.5980	2146.63	913.19
	C.S.M.		0.8389	0.8530	-	-

1 The quantities in the parentheses are the units of the parameters.

*H.M.R. = Hybrid Mixing Rules
C.S.M. = Conformal Solution Model

Table VI.5

Results of Vapor-liquid Equilibrium Predictions for Nonpolar-Polar Binary Systems

Systems (1) - (2)	Model	T K	ρ^{g}	% AARD K_1	K_2	X_1	X_2	Y_1	Y_2
Hydrocarbons and Ketones									
Ethane-Acetone	H.M.R.			3.14	11.70	3.25	8.92	0.26	13.38
	C.S.M.			7.98	43.63	11.11	24.13	0.27	14.50
Acetone-Cyclohexane	H.M.R.			4.95	6.10	3.22	4.36	3.33	9.52
	C.S.M.			18.35	84.14	13.41	30.27	19.82	28.75
Cyclohexane-2-Butanone	H.M.R.		0.081	1.02	5.61	2.61	8.27	2.05	3.92
	C.S.M.		23.88	7.84	5.41	9.68	8.72	5.46	6.07
Hydrocarbons and Aniline									
Cyclohexane-Aniline	H.M.R.			6.10	10.81	6.50	11.86	0.07	6.01
	C.S.M.			10.73	21.01	11.41	20.44	0.12	9.68

Table VI.5 (Continued)

Systems (1) - (2)	Model	T / K	ε / ρ	% AARD K 1	K 2	X 1	X 2	Y 1	Y 2
Toluene-Aniline	H.M.R.			0.86	1.96	0.86	1.85	0.17	1.88
	C.S.H.			0.58	1.74	0.57	1.60	0.16	1.82
Benzene-Aniline	H.M.R.			1.02	4.55	1.04	4.38	0.06	6.54
	C.S.H.			1.07	4.82	1.09	4.43	0.07	6.80
Methylcyclo hexane-Aniline	H.M.R.			3.62	6.24	3.77	7.40	0.12	2.52
	C.S.H.			7.74	11.70	8.37	12.14	0.20	4.42
Hydrocarbons and Alcohols									
Methanol-Benzene	H.M.R.	298.15	1.27	2.91	3.28	3.11	4.48	0.87	1.16
	C.S.H.		18.12	22.15	18.76	58.50	20.98	19.50	21.09
	H.M.R.	308.15		4.84	3.54	4.62	5.14	2.17	3.13
	C.S.H.			20.16	22.72	30.18	22.18	18.79	20.19
	H.M.R.	328.15		3.51	2.96	2.48	1.81	1.44	2.30
	C.S.H.			20.35	17.12	28.78	21.16	15.70	20.15
Methanol-n-Heptane	H.M.R.			2.34	9.04	1.41	5.21	1.65	5.32
	C.S.H.			20.80	26.17	25.18	14.18	14.18	19.83

Table VI.5 (Continued)

Systems (1) - (2)	Model	T K	% AARD ρ^{ε}	K_1	K_2	X_1	X_2	Y_1	Y_2
Methanol-Toluene	H.M.R.		2.57	3.05	12.80	2.90	11.14	0.66	5.81
	C.S.M.		38.72	32.68	43.00	41.92	30.08	6.26	10.06
Methanol-1-Methyl naphthalene	H.M.R.			4.03	10.81	4.47	12.66	0.66	12.72
	C.S.M.			12.03	30.05	13.31	21.60	0.69	9.50
n-Hexane-Ethanol	H.M.R.	298.15		4.70	15.94	4.75	12.68	2.13	5.39
	C.S.M.			23.69	46.07	36.01	25.97	15.96	16.22
	H.M.R.	318.15		4.06	12.08	4.21	9.44	1.15	3.11
	C.S.M.			22.69	42.17	21.85	26.16	10.34	22.93
	H.M.R.	328.15		2.72	6.91	2.68	5.27	3.20	5.85
	C.S.M.			21.26	27.29	23.45	41.03	17.83	14.12
Ethanol-Cyclohexane	H.M.R.	298.15		3.79	3.92	1.71	2.70	3.19	2.06
	C.S.M.			32.30	19.58	39.87	25.23	18.42	10.70
	H.M.R.	323.15		2.79	3.04	1.35	3.17	2.13	1.90
	C.S.M.			76.76	27.32	39.73	32.05	14.43	16.80
Benzene-Ethanol	H.M.R.	298.15		3.09	6.11	1.26	3.67	2.90	4.01
	C.S.M.			8.12	13.81	8.12	27.02	6.18	12.00
	H.M.R.	328.15		3.63	5.24	3.44	6.89	1.44	2.98
	C.S.M.			7.17	12.72	7.23	26.68	6.32	11.98

Table VI.5 (Continued)

Systems (1) - (2)	Model	T K	ε/ρ	% AARD K 1	K 2	X 1	X 2	Y 1	Y 2
Ethanol-Toluene	H.M.R.		2.24	1.84	5.18	1.17	4.94	1.32	4.46
	C.S.M.		36.31	20.15	32.97	15.19	51.35	7.37	14.39
Benzene-n-Propanol	H.M.R.	298.15		1.09	3.21	1.16	1.76	0.75	2.87
	C.S.M.			10.79	17.66	11.39	13.79	5.07	5.80
	H.M.R.	318.15		2.01	6.81	1.19	2.68	1.54	5.07
	C.S.M.			7.66	15.61	8.85	14.19	1.78	5.25
Cyclohexane-n-Propanol	H.M.R.	298.15		1.14	2.23	1.01	1.43	0.55	2.62
	C.S.M.			17.92	36.92	18.65	18.54	7.50	8.58
	H.M.R.	328.15		7.09	11.68	6.73	6.73	2.05	3.30
	C.S.M.			13.76	25.94	14.98	41.52	10.50	14.42
n-Propanol-n-Heptane	H.M.R.		3.03	0.63	11.87	3.68	8.89	2.35	2.47
	C.S.M.		21.07	12.53	10.40	21.85	12.01	11.71	11.65
Toluene-n-Butanol	H.M.R.	363.15		5.41	4.70	2.90	2.73	5.05	3.53
	C.S.M.			5.80	5.44	4.39	5.51	6.34	6.47
	H.M.R.	373.15		1.81	1.43	1.77	2.02	1.72	2.19
	C.S.M.			2.39	2.96	2.20	3.33	2.82	2.94

Table VI.5 (Continued)

Systems (1) - (2)	Model	T K	ρ^G	% AARD K_1	K_2	X_1	X_2	Y_1	Y_2
Benzene-n-Butanol	H.M.R.			4.31	7.37	5.91	8.26	2.24	10.23
	C.S.M.			6.19	11.13	7.56	11.04	2.19	12.91
Hydrocarbons and Phenol									
Benzene-Phenol	H.M.R.			1.73	11.49	1.79	6.88	0.13	9.21
	C.S.M.			3.53	8.27	3.63	10.73	0.15	13.24
n-Decane-Phenol	H.M.R.			6.50	11.68	7.38	13.36	3.47	8.68
	C.S.M.			13.21	31.52	23.99	67.64	8.26	21.51
Hydrocarbons and water									
Methane-Water	H.M.R.	310.92		1.95	4.78	1.97	0.004	0.005	4.78
	C.S.M.			8.20	11.10	9.70	0.03	0.01	11.08
	H.M.R.	344.26		1.92	1.93	1.98	0.004	0.008	1.93
	C.S.M.			9.51	7.59	11.45	0.03	0.03	7.56
	H.M.R.	377.60		1.56	1.16	1.55	0.003	0.02	1.16
	C.S.M.			9.32	4.99	11.40	0.04	0.06	4.96

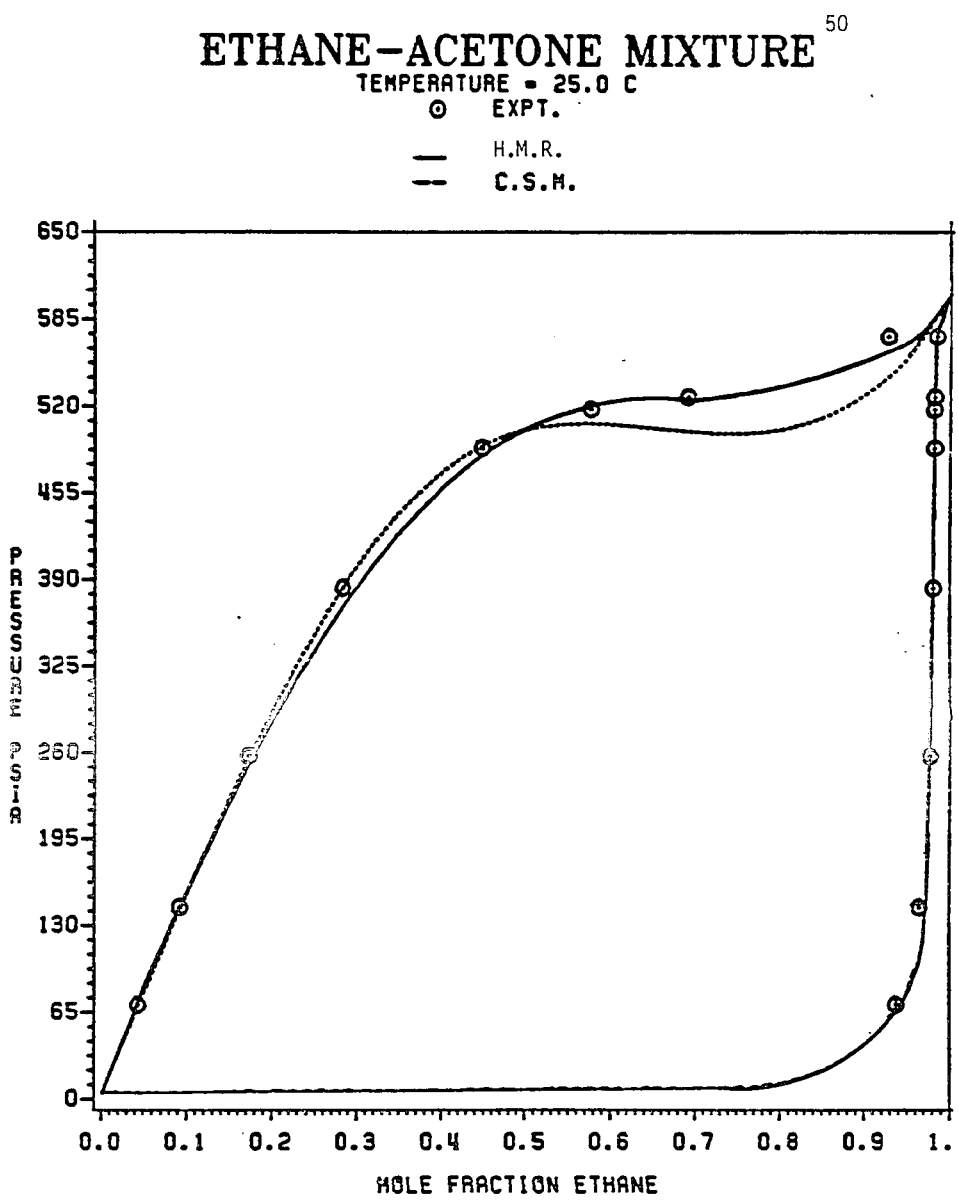
Table VI.5 (Continued)

Systems (1) - (2)	Model	T K	ρ^{G}	% AARD K_1	K_2	X_1	X_2	Y_1	Y_2
Methane-Water	H.M.R.	410.93		2.46	3.26	2.43	0.003	0.19	3.27
	C.S.M.			7.70	4.83	8.00	0.03	0.12	4.10
	H.M.R.	444.26		1.20	4.74	1.41	0.003	0.66	4.74
	C.S.M.			7.92	4.12	9.11	0.005	0.36	4.10
Ethane-Water	H.M.R.	344.26		2.29	7.11	2.38	0.002	0.03	7.11
	C.S.M.			17.35	18.98	25.08	0.02	0.08	18.96
	H.M.R.	373.60		3.71	5.09	3.84	0.004	0.07	5.09
	C.S.M.			16.14	15.08	21.38	0.02	0.19	15.06
	H.M.R.	410.93		6.77	3.39	6.68	0.008	0.19	3.40
	C.S.M.			16.78	12.88	23.64	0.01	0.33	12.83
	H.M.R.	444.26		12.22	3.47	11.03	0.01	0.69	3.48
	C.S.M.			13.50	16.06	17.30	0.04	0.68	15.59

[G] One set of parameters was used to calculate the density for total temperature range of density data

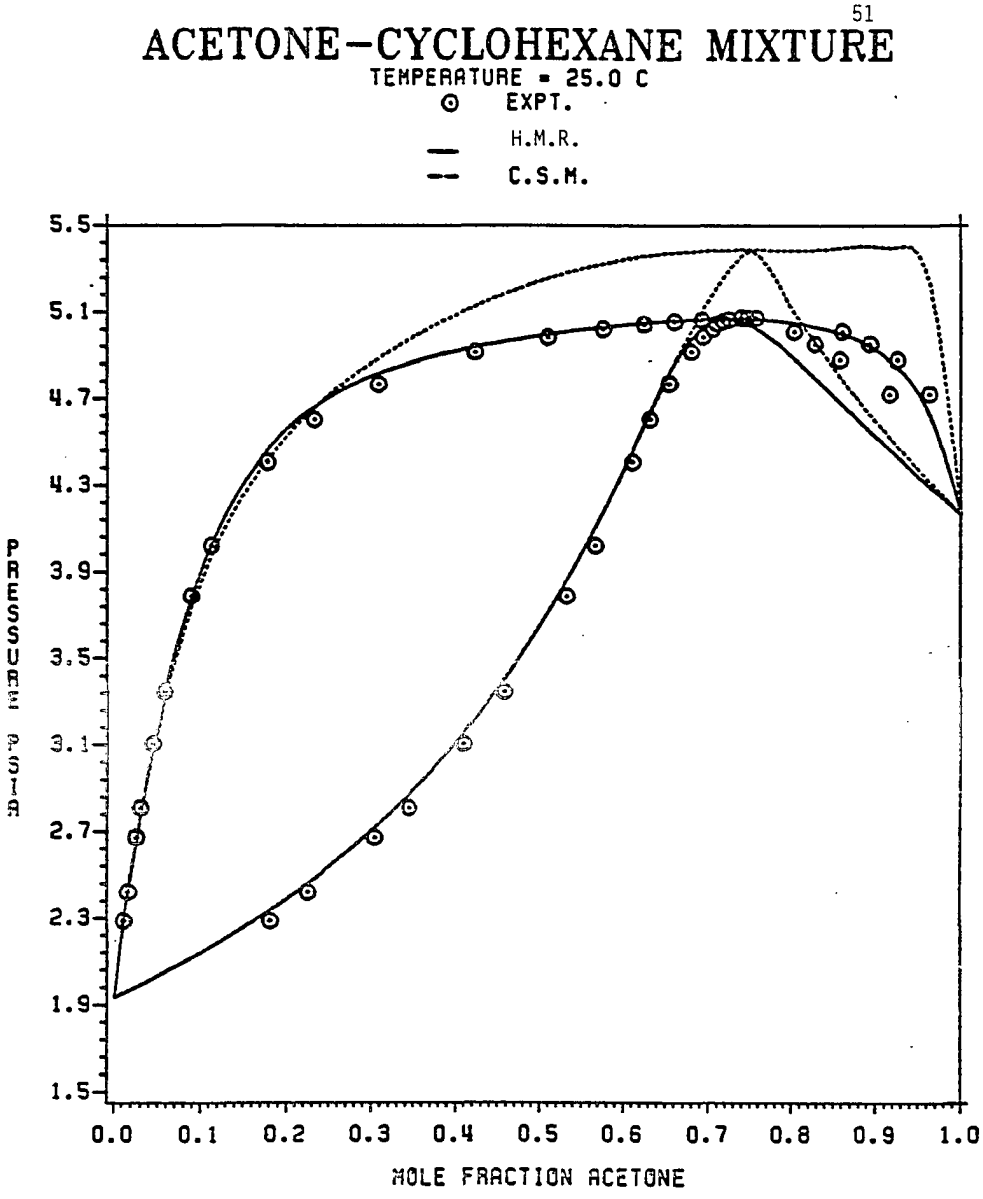
[#]

$$\% \text{ AARD} = \frac{\Sigma (|\text{calc} - \text{exp}| / \text{exp}) \times 100}{N}$$



THE P-X DIAGRAM OF THE ETHANE-ACETONE SYSTEM AT 25.0 C

FIGURE 3



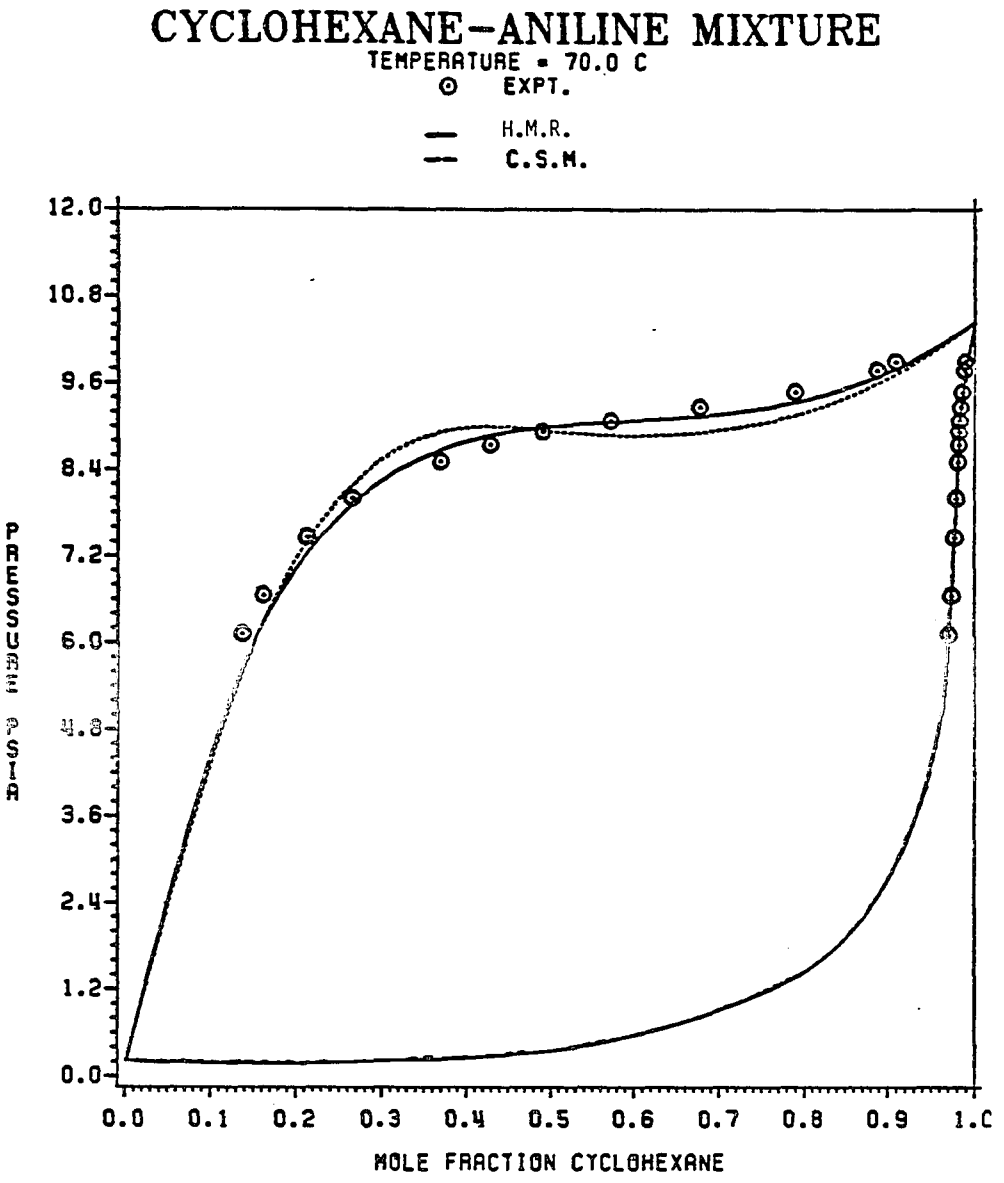
THE P-X DIAGRAM OF THE ACETONE-CYCLOHEXANE SYSTEM AT 25.0 C

FIGURE 4

Although the CSM could also describe the azeotropic phase behavior, it predicted an azeotrope at wrong conditions. For cyclohexane-2-butanone system, in addition to VLE, the mixture density was also calculated. The CSM gives poor results for both VLE and density. For mixture density the % AARD from the CSM is 23.8 % and from HMR is 0.08 %. The agreement in density prediction from HMR is gratifying when no experimental density data were used to obtained the binary parameters.

Figure 5 shows a representative nonideal systems of hydrocarbons with aniline. Again good fits were obtained by the HMR. Toluene-Aniline and Benzene-Aniline systems are ideal solutions. These mixtures contain molecules similar in size and shape, the only difference is their polarities. Both types of mixing rules fitted the VLE data very well (see table VI.5). There is a significant change in the nonideality of the cyclohexane-aniline system compared with benzene-aniline or toluene-aniline systems, since cyclohexane is a cyclic aliphatic hydrocarbon and benzene, toluene and aniline are aromatic compounds.

Hydrocarbon-alcohol mixtures are typically strongly nonideal solutions. The alcohols represent an important group of polar and associating compounds. Most of these binary mixtures have azeotropes. These systems are difficult to correlate. For the systems with azeotropic phase behavior, the binary parameters are temperature dependent. It is not possible to use one set of binary

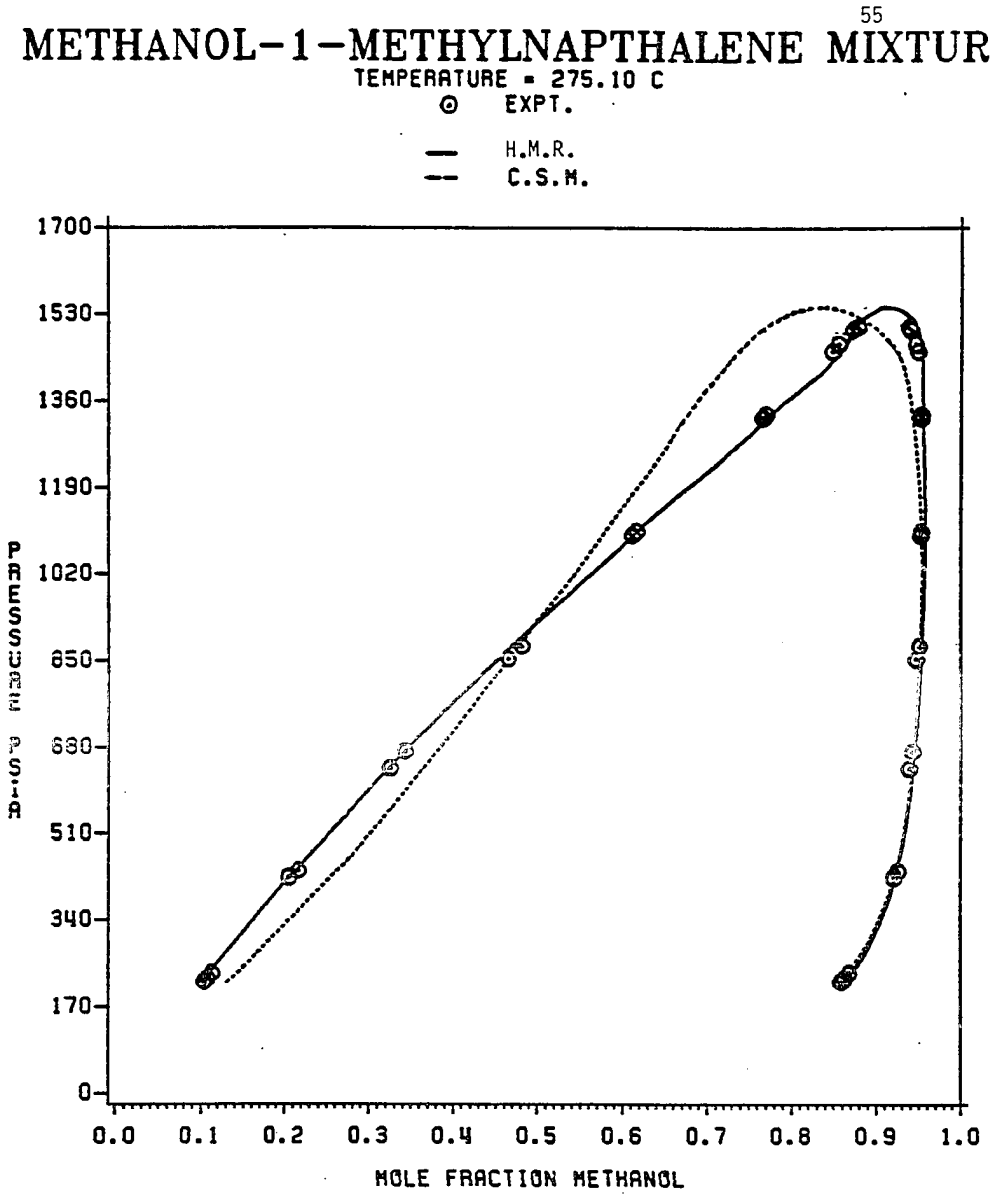


THE P-X DIAGRAM OF THE CYCLOHEXANE-ANILINE SYSTEM AT 70.0 C

FIGURE 5

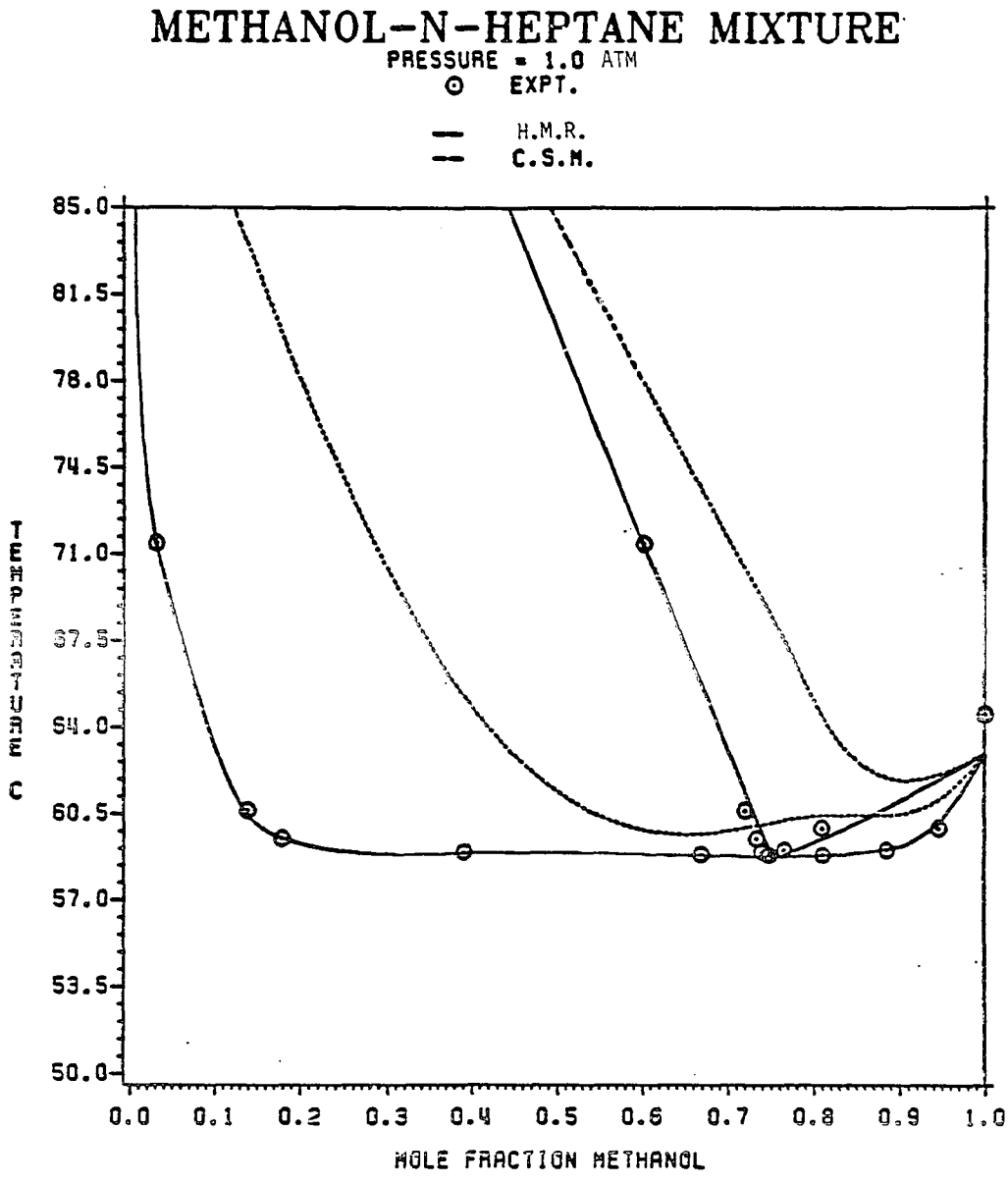
parameters over a wide range of temperature with the exception of methanol-1-methylnapthalene system which posses no azeotropic phase behavior, one set of parameter was used for all temperature range (see Figure 6). However, with temperature dependent parameters, the HMR represented well these nonideal mixtures (see table VI.5). For methanol-benzene, methanol-toluene and n-propanol- n-heptane systems, the mixture densities were also well predicted by the HMR. Good agreement can be obtained for mixture density of methanol-benzene systems by using one set of parameter over a wide range of temperature in contrast to VLE property. Figure 7 shows results for nonideal system (methanol-n-heptane) with minimum boiling temperature. Figures 8 and 9 show results of nonideal mixtures (n-hexane-ethanol, cyclohexane-n-propanol) with maximum vapor pressure. For these systems the HMR gives accurate results for all composition ranges. On the other hand the CSM is totally inadequate for representing such highly nonideal systems. Figure 7 also shows the VLE calculations, near the concentrated methanol compositions, are strongly affected when the pure methanol calculated vapor pressure is in error. The improvement can be made by redetermining the pure equation of state parameters to match the experimental vapor pressure at this particular temperature.

For mixtures of hylrocarbons and phenol, two binary mixtures including benzene-phenol and n-decane-phenol systems were tested. Figure 10 shows results for n-decane-



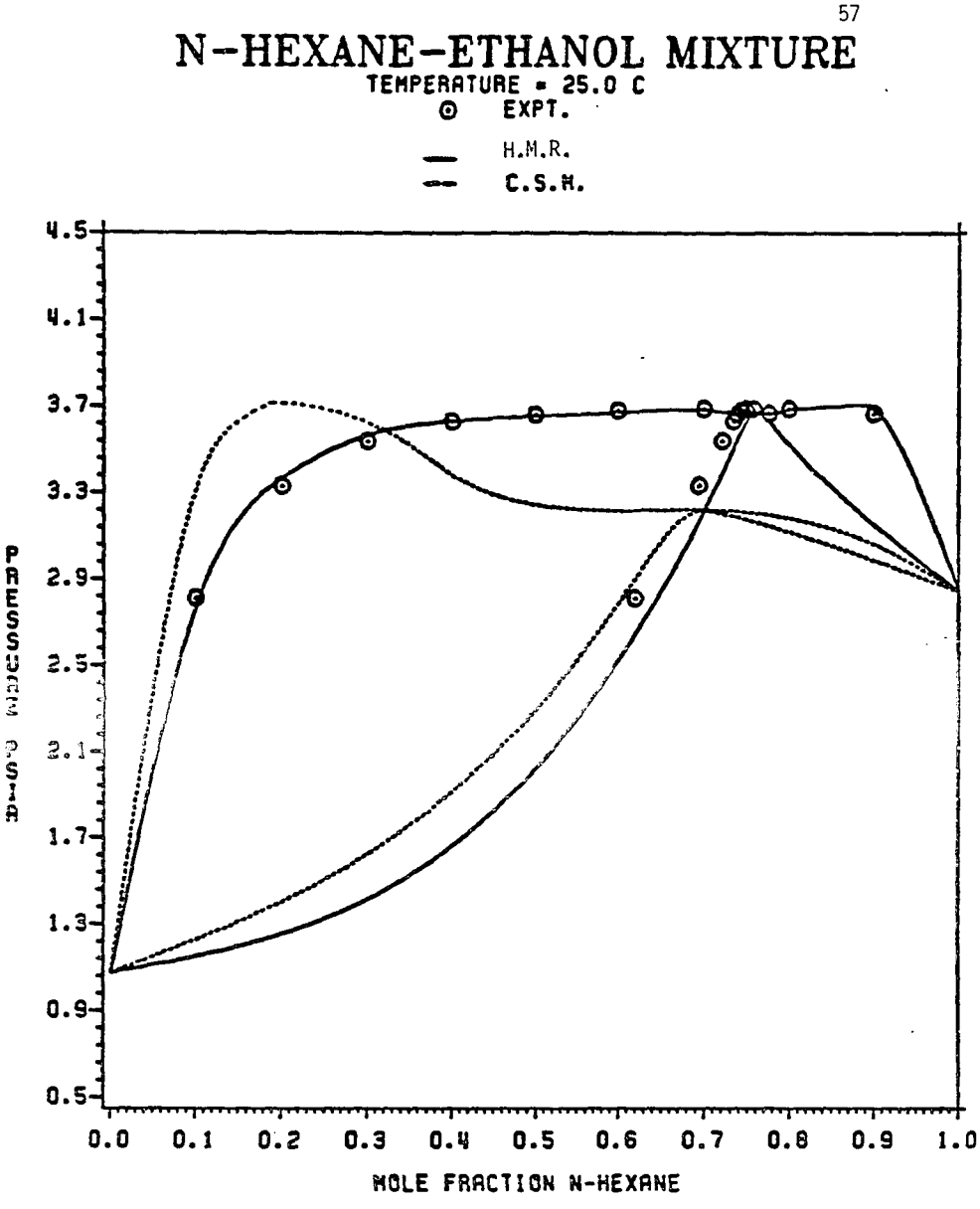
THE P-X DIAGRAM OF THE METHANOL-1-METHYLNAPTHALENE SYSTEM AT 275.10 C

FIGURE 6



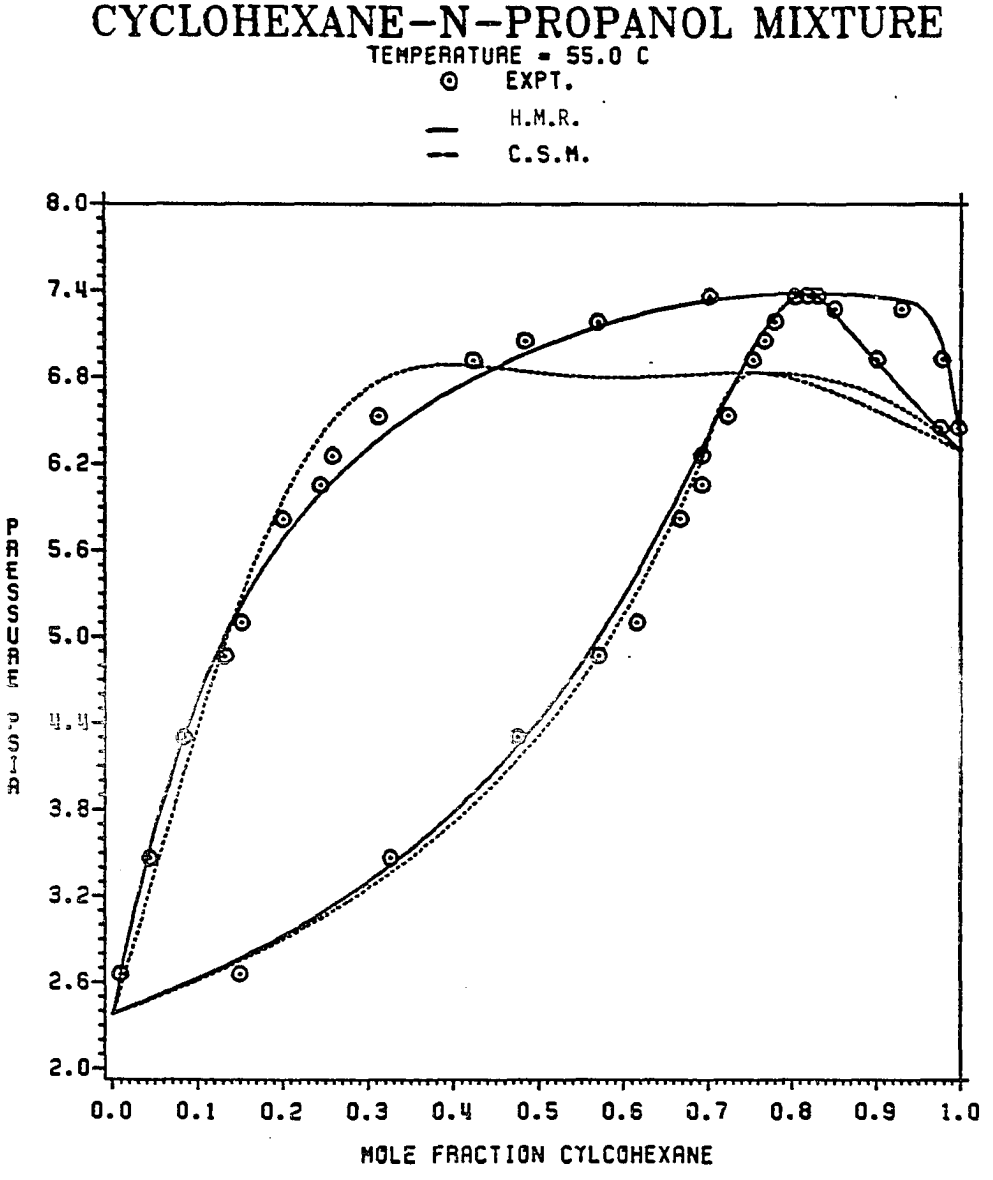
THE T-X DIAGRAM OF THE METHANOL-N-HEPTANE SYSTEM AT ATMOSPHERIC PRESSURE

FIGURE 7



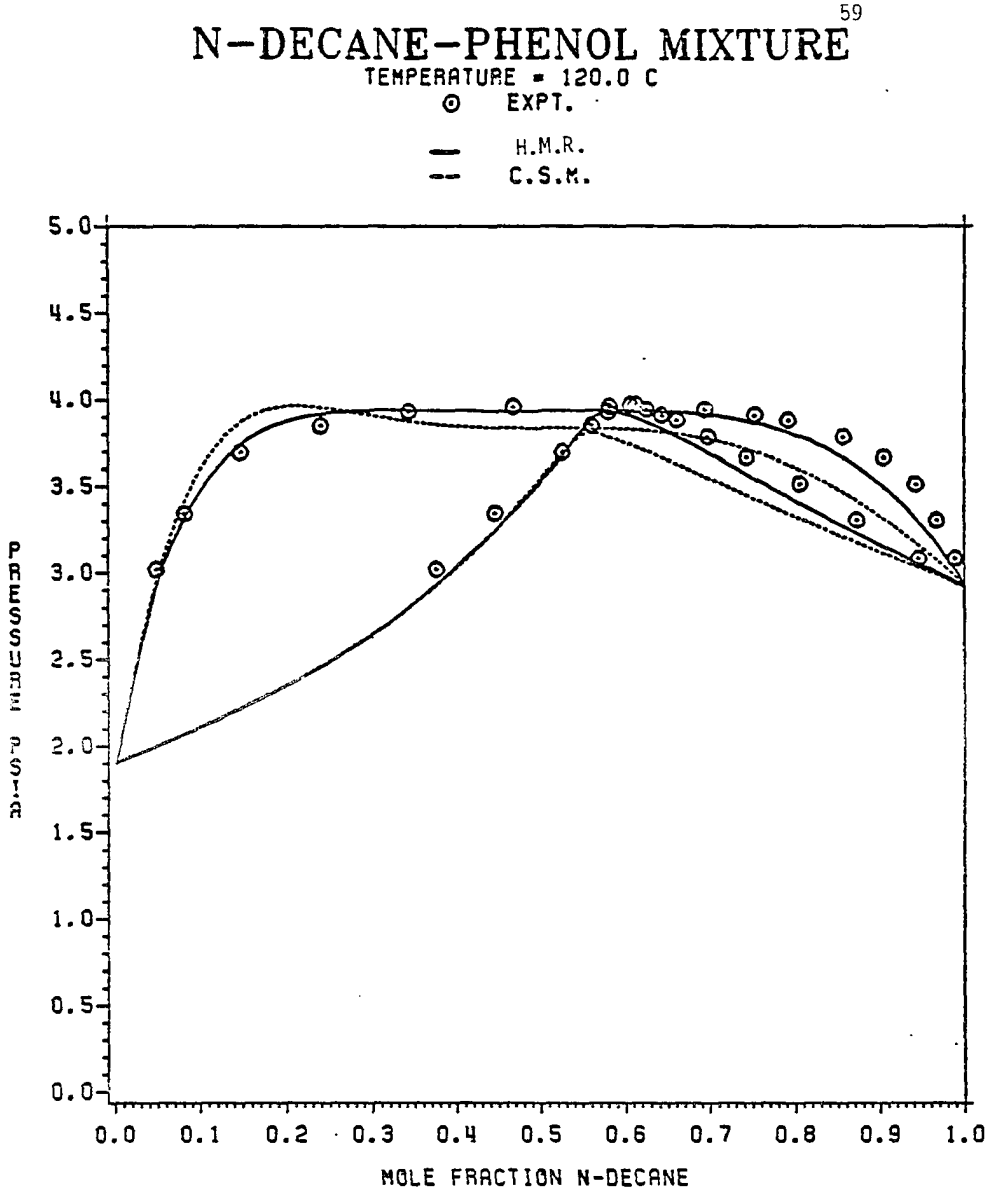
THE P-X DIAGRAM OF THE N-HEXANE-ETHANOL SYSTEM AT 25.0 C

FIGURE 8



THE P-X DIAGRAM OF THE CYLCOHEXANE-N-PROPANOL SYSTEM AT 55.0 C

FIGURE 9



THE P-X DIAGRAM OF THE N-DECANE-PHENOL SYSTEM AT 120.0 C

FIGURE 10

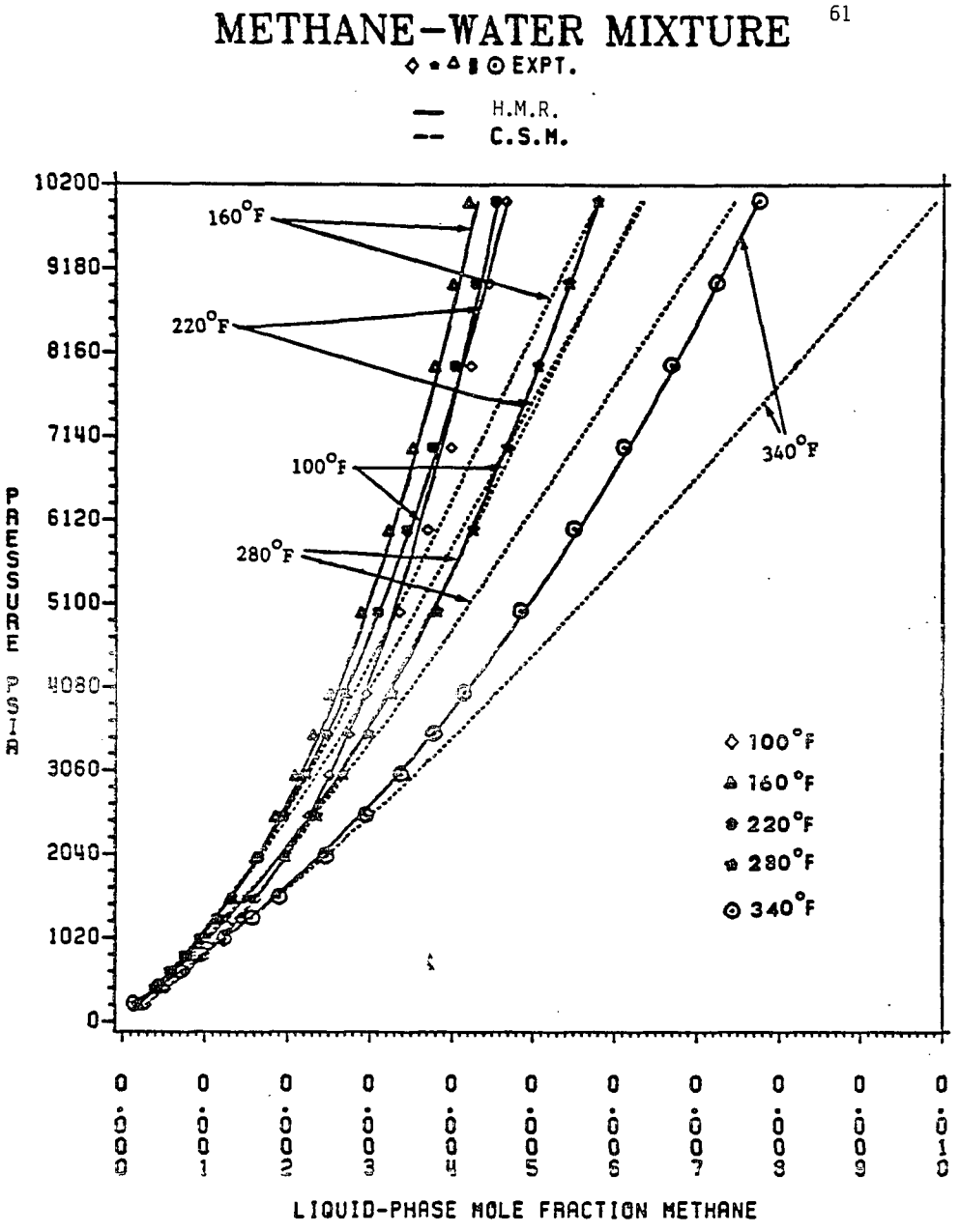
phenol mixture with maximum azeotropic pressure. The phase behavior of these nonideal systems were quite well represented by the HMR.

The methane-water system shown in Figures 11-12 is another strongly nonideal system. Figure 11 shows the saturated-liquid compositions for methane-water system at elevated pressure. The HMR gives better predictions than the CSM. As shown in Figure 12, at constant pressure, the minimum solubility of methane in water occurs within the temperature range. This minimum exists at 160 F. The HMR is able to reproduce this phase behavior. Figure 13 shows the experimental and calculated VLE for ethane-water system. The HMR predicted VLE for this system with reasonable accuracy. The results for this system are less accurate than those for methane-water mixtures, since ethane is less soluble in water than methane.

Overall, the HMR was applied with satisfactory results for nonpolar-polar binary systems, while the CSM yields poor results for these nonideal systems.

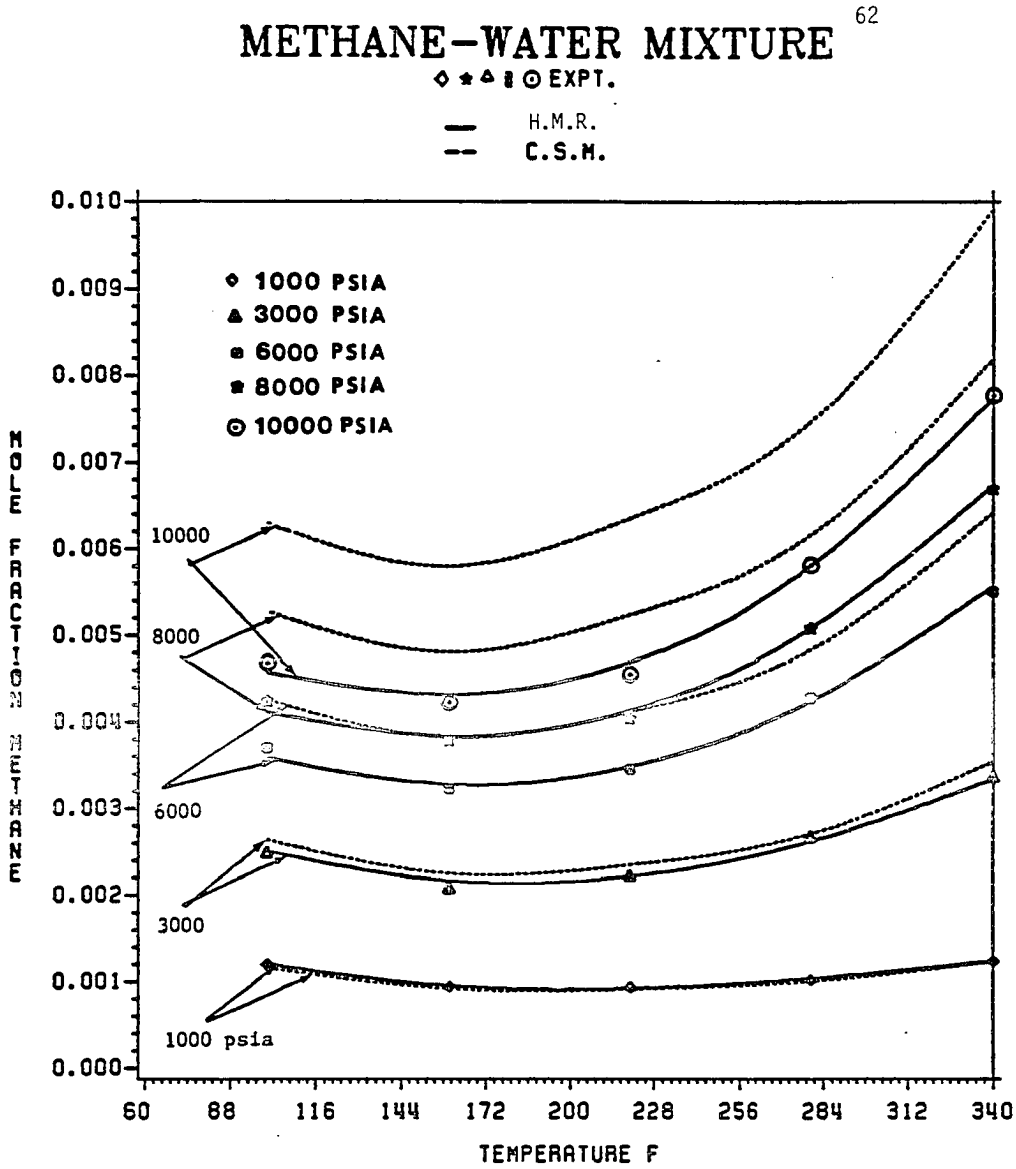
6.2 Application to Polar-Polar Binary Systems

The HMR also was applied to mixtures containing only polar and/or associating compounds. Table VI.6 lists ten such binary systems studied in this work. The binary parameters determined from VLE data are reported in table VI.7. A summary of results is presented in table VI.8. The



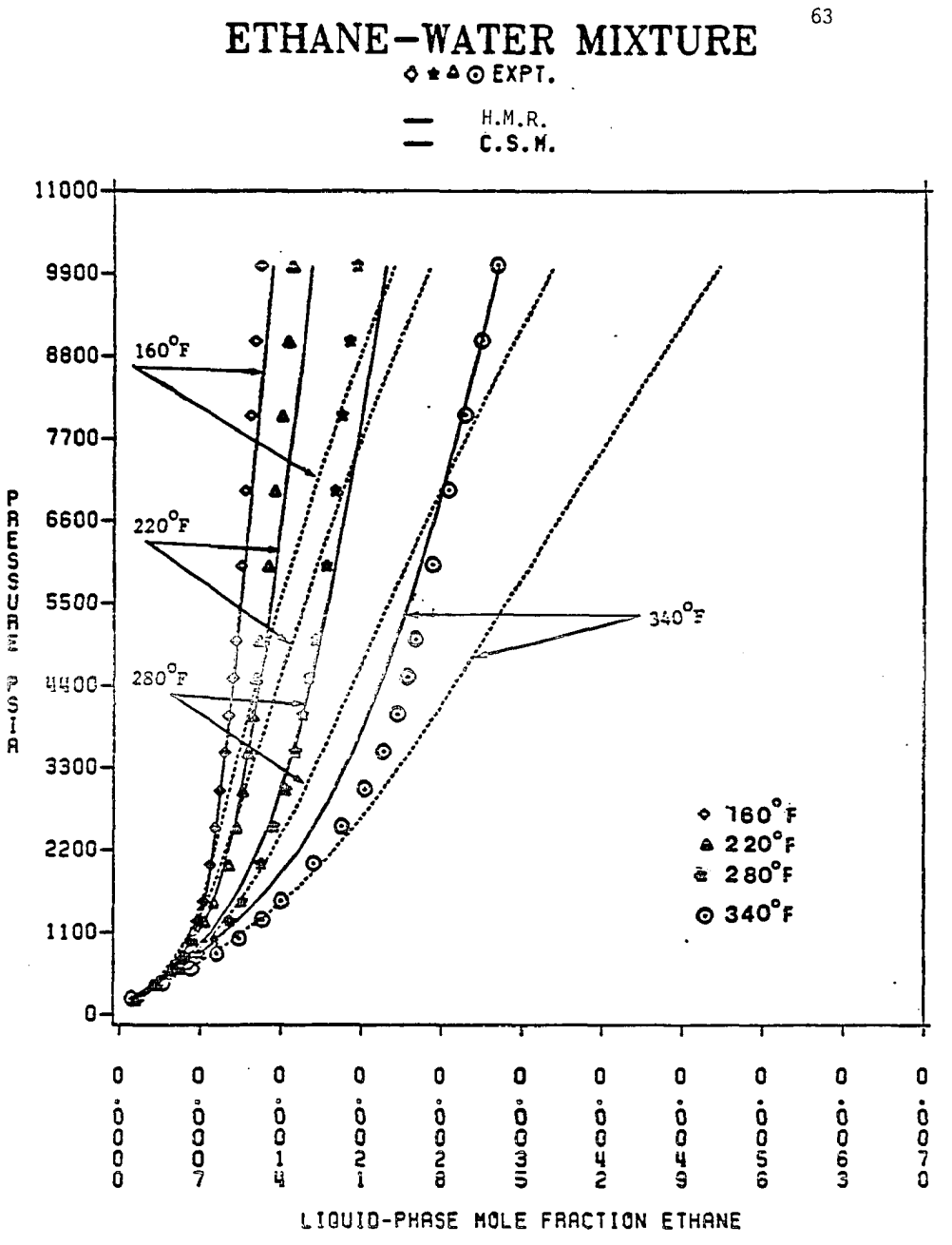
SATURATED-LIQUID COMPOSITIONS IN METHANE-WATER SYSTEM

FIGURE 11



SOLUBILITY OF METHANE IN WATER AT CONSTANT PRESSURE

FIGURE 12



SATURATED-LIQUID COMPOSITIONS IN ETHANE-WATER SYSTEM

FIGURE 13

Table VI.6

Temperature and Pressure Ranges, and Data References for the Polar - Polar Binary Systems Studied in This Work.

Systems (1) -- (2)	Pro.	No. of points	T range K	P range atm	Data References
Carbon dioxide-Methanol	VLE	29	298-313	2.15-76.0	Katayama et al. 1975 Ohgaki et al. 1976
Diethyl Ether-Methanol	VLE	28	303-329	0.24-0.92	Gmehling et al. 1980
Tetrahydrofuran-n-Propanol	VLE	11	345-367	1	Yoshikawa et al. 1980
n-Propanol-n-Butanol	VLE	7	373-388	1	Gay 1927
Acetone-Water	VLE	75	373-523	1.09-66.6	Griswold et al. 19
Hydrogen Sulfide-Water	VLE	47	310-444	100-3000	Selleck et al. 1952
Water-Pyridine	VLE VLE	13 28	323 343-363	0.10-0.15 0.23-0.85	Ihl et al. 1954 Audon et al. 1957
Methanol-Water	VLE ρ	137 55	298-416 298-323	0.05-5.00 1	Gmehling et al. 1977a Mikhail et al. 1961
Water-n-Butanol	VLE	20	365-387	1	Kato et al. 1970
Water-Phenol	VLE	22	317	0.01-0.09	Weller et al. 1963

Table VI.7

Binary Interaction Parameters for Polar-Polar Binary Systems

Systems (1) - (2)	Model	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
Carbon Dioxide-Methanol	H.M.R.		1.0000	0.9265	-568.21	1528.33
	C.S.M.		0.9859	1.0081	-	-
Diethyl Ether-Methanol	H.M.R.		1.0000	0.9334	910.45	982.05
	C.S.M.		0.9693	1.0204	-	-
Tetrahydrofuran-n-Propanol	H.M.R.		0.9745	0.9965	0.0	0.0
	C.S.M.		0.9967	0.9790	-	-
n-Propanol-n-Butanol	H.M.R.		0.9910	0.9983	0.0	0.0
	C.S.M.		1.0014	0.9942	-	-
Acetone-Water	H.M.R.	373.15	1.0000	0.9428	406.18	-411.05
	C.S.M.		0.9967	1.0543	-	-
	H.M.R.	423.15	1.0000	0.9312	611.93	-613.05
	C.S.M.		0.9870	1.0404	-	-
	H.M.R.	473.15	1.0000	0.9288	790.50	-823.29
	C.S.M.		0.9756	1.0320	-	-
	H.M.R.	523.15	1.0000	0.9192	1038.92	-1045.86
	C.S.M.		0.9688	1.0218	-	-

Table VI.7 (Continued)

Systems (1) - (2)	Model	T (K)	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
Hydrogen Sulfide-Water	H.M.R.		0.8568	1.0000	-403.83	215.21
	C.S.M.		0.9528	1.0880	-	-
Water-Pyridine	H.M.R.	323.15	1.0000	0.9751	-1286.53	-2424.18
	C.S.M.		0.9755	0.9925	-	-
	H.M.R.	343.00	1.0000	0.9671	-1334.98	-1327.86
	C.S.M.		0.8796	1.0154	-	-
	H.M.R.	363.00	1.0000	0.9609	-1429.19	-1230.63
	C.S.M.		0.9263	0.9874	-	-
Methanol-Water	H.M.R.		1.0000	0.9542	-1257.73	186.89
	C.S.M.		1.0075	1.0300	-	-
Water-n-Butanol	H.M.R.		1.0000	0.9128	-1596.57	-2299.98
	C.S.M.		0.6945	1.1143	-	-
Water-Phenol	H.M.R.		1.0000	0.8650	-1489.32	6628.10
	C.S.M.		1.2574	0.9125	-	-

Table VI.8

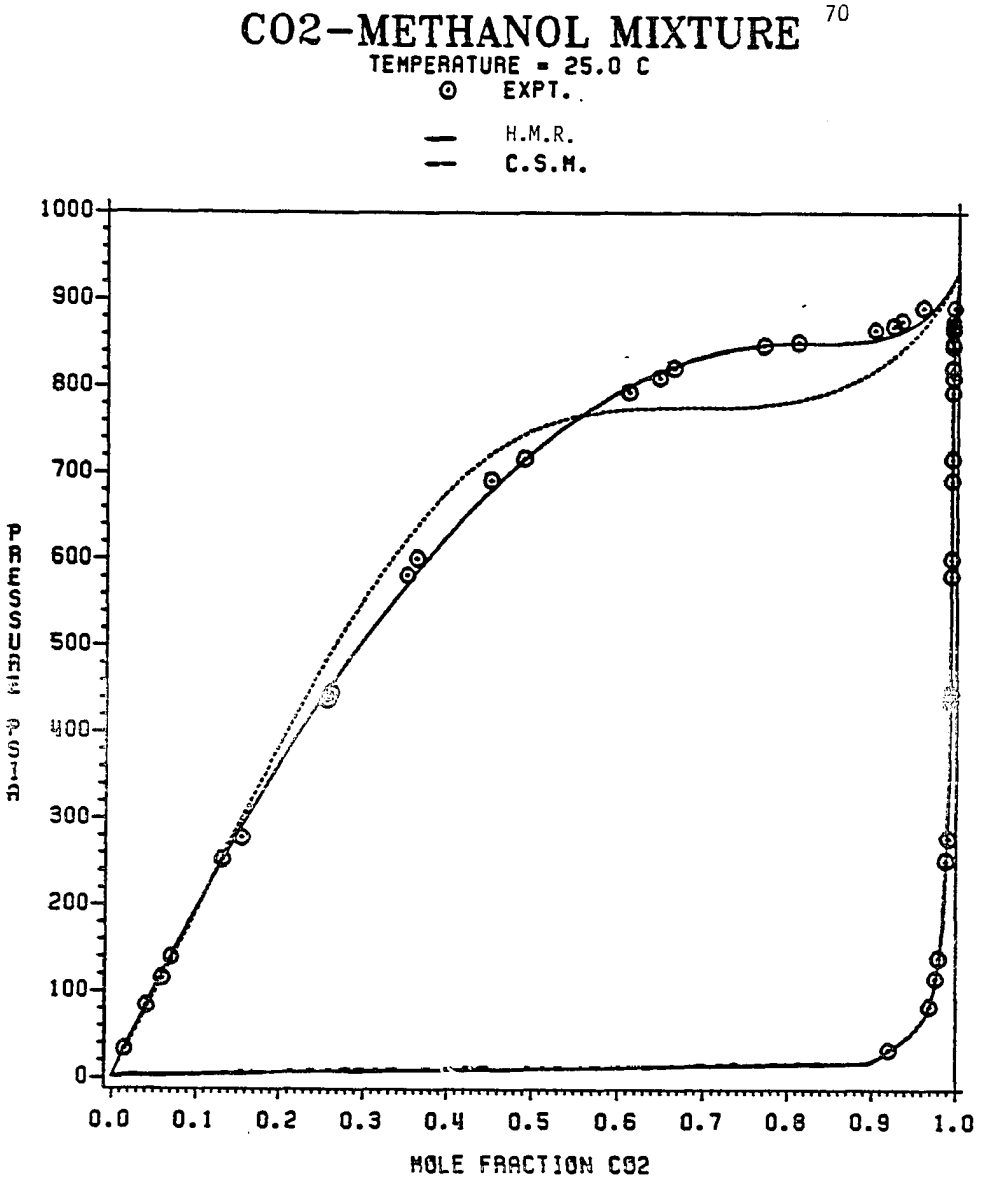
Results of Vapor-Liquid Equilibrium Predictions for Polar-Polar Binary Systems

Systems (1) - (2)	Model	T K	P	% AARD K_1	% AARD K_2	% AARD X_1	% AARD X_2	% AARD Y_1	% AARD Y_2
Carbon Dioxide-Methanol	H.M.R.			3.26	9.39	3.60	6.30	0.09	9.71
	C.S.M.			10.34	43.48	12.00	22.78	0.11	11.55
Diethyl Ether-Methanol	H.M.R.			5.09	6.84	5.52	8.52	1.76	3.94
	C.S.M.			7.55	9.26	8.26	10.32	2.26	10.00
Tetrahydrofuran-n-Propanol	H.M.R.			0.52	6.22	2.50	1.45	2.66	7.49
	C.S.M.			0.57	6.37	2.57	1.47	2.71	7.69
n-Propanol-n-Butanol	H.M.R.			0.03	2.87	3.05	2.61	3.05	5.60
	C.S.M.			0.03	3.02	3.17	2.74	3.17	5.89
Acetone-Water	H.M.R.	373.15		6.42	3.10	8.33	3.30	2.28	1.65
	C.S.M.			23.43	31.01	19.41	18.44	19.12	22.68
	H.M.R.	423.15		6.43	6.67	5.20	5.97	1.82	1.80
	C.S.M.			21.07	29.82	21.09	18.43	15.07	26.80
	H.M.R.	473.15		3.22	3.83	6.75	4.34	4.34	2.28
	C.S.M.			20.58	32.74	20.57	19.60	20.16	21.82

Table VI.8 (Continued)

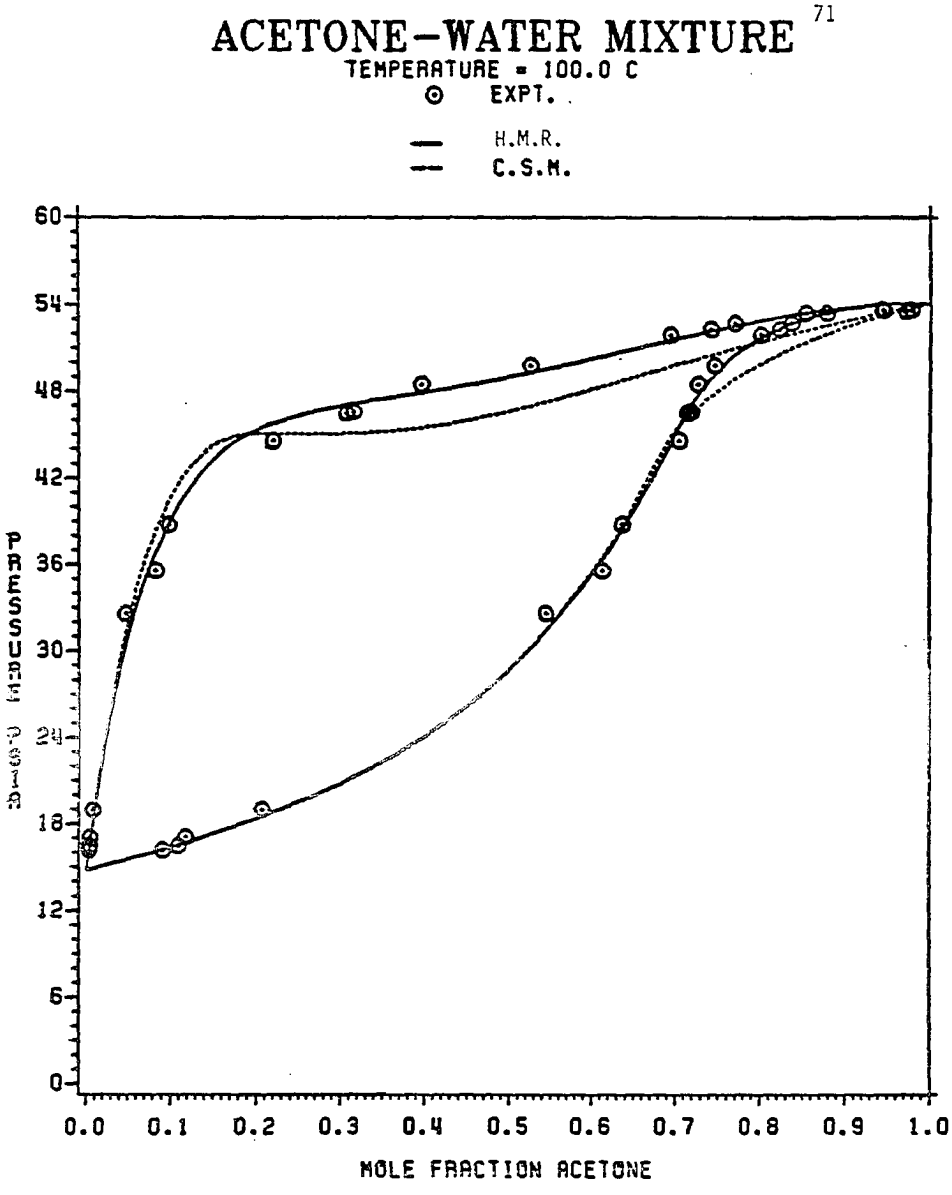
Systems (1) - (2)	Model	T K	ρ	% AARD K 1	K 2	X 1	X 2	Y 1	Y 2
Acetone-Water	H.M.R.	523.15		9.41	2.55	7.00	2.01	4.16	0.96
	C.S.M.			27.74	31.70	28.37	22.14	18.20	24.42
Hydrogen Sulfide-Water	H.M.R.			6.40	8.12	6.38	0.31	0.54	8.29
	C.S.M.			10.23	11.84	21.58	0.61	0.84	11.94
Water-Pyridine	H.M.R.	323.15		2.21	7.52	3.02	13.02	1.84	4.58
	C.S.M.			9.93	22.06	23.48	12.67	11.70	7.92
	H.M.R.	343.00		2.21	5.27	2.13	5.42	1.29	3.04
	C.S.M.			9.46	15.41	15.41	31.92	9.92	17.82
	H.M.R.	363.00		1.26	5.60	1.48	6.86	1.12	1.88
	C.S.M.			10.06	11.26	23.99	16.92	9.72	10.37
Methanol-Water	H.M.R.		1.60	4.74	7.34	7.36	6.67	3.49	9.31
	C.S.M.		1.88	4.80	6.36	7.35	9.45	3.38	10.70
Water-n-Butanol	H.M.R.			3.56	14.81	2.94	10.28	1.76	5.23
	C.S.M.			18.59	30.45	19.29	30.46	18.57	31.10
Water-Phenol	H.M.R.			7.58	19.16	7.08	15.22	0.18	9.86
	C.S.M.			26.40	76.83	44.39	84.86	0.88	58.12

data correlation can be significantly improved by using the HMR. Figure 14 shows good agreement between experiment and calculated compositions using the HMR for carbon dioxide-methanol system. The carbon dioxide molecules and methanol molecules are different in size, shape and polarity. Therefore the mixture of these components produces exotic phase behavior. In Figure 14, the CSM fails badly when the nonideality occurs at the composition of CO2 greater than 0.6. Good fits were obtained at both 25 C and 40 C using the HMR with one set of parameters. Figures 15-18 show the results for acetone-water system at four temperature. The HMR yields accurate results up to the critical point for this nonideal system with azeotropes. As shown in theses figures the CSM has a tendency towards predicting false phase-splitting. Similar observation was also noted by Huron and Vidal (1979). Figures 19 and 20 show water-n-butanol and water-phenol systems. The same patterns can be seen in these figures. Good predictions were obtained from the HMR, poor predictions were obtained from the CSM. Though tetrahydrofuran-n-propanol, n-propanol-n-butanol, and methanol-water systems contain polar and associating compounds, these mixtures are only slightly nonideal. The ideality of these systems is reflected in their activity coefficients. The activity coefficients of these components in the mixture do not differ substantially from unity. As a result, both types of mixing rules give good predictions for VLE and mixture density (see table VI.8).



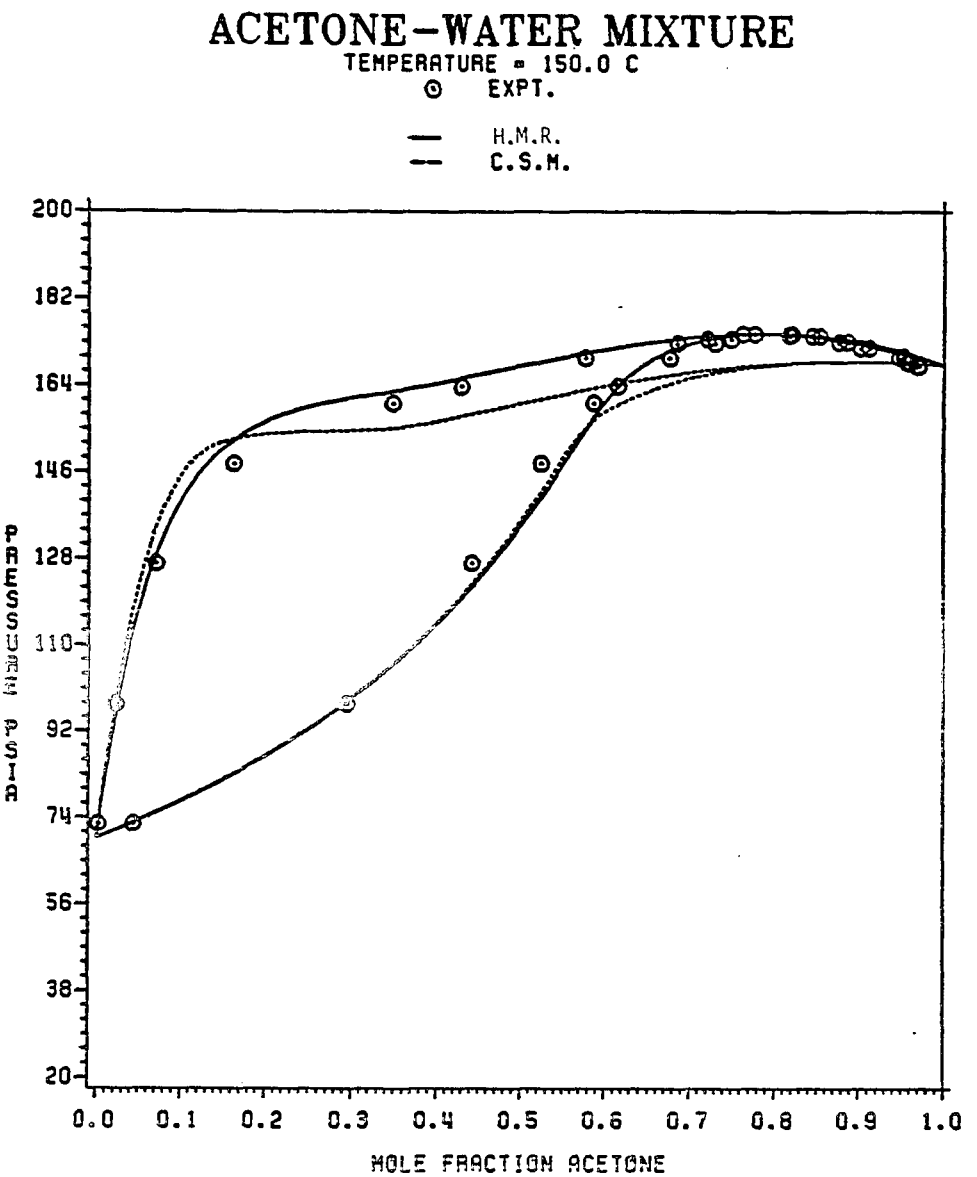
THE P-X DIAGRAM OF THE CO2-METHANOL SYSTEM AT 25.0 C

FIGURE 14



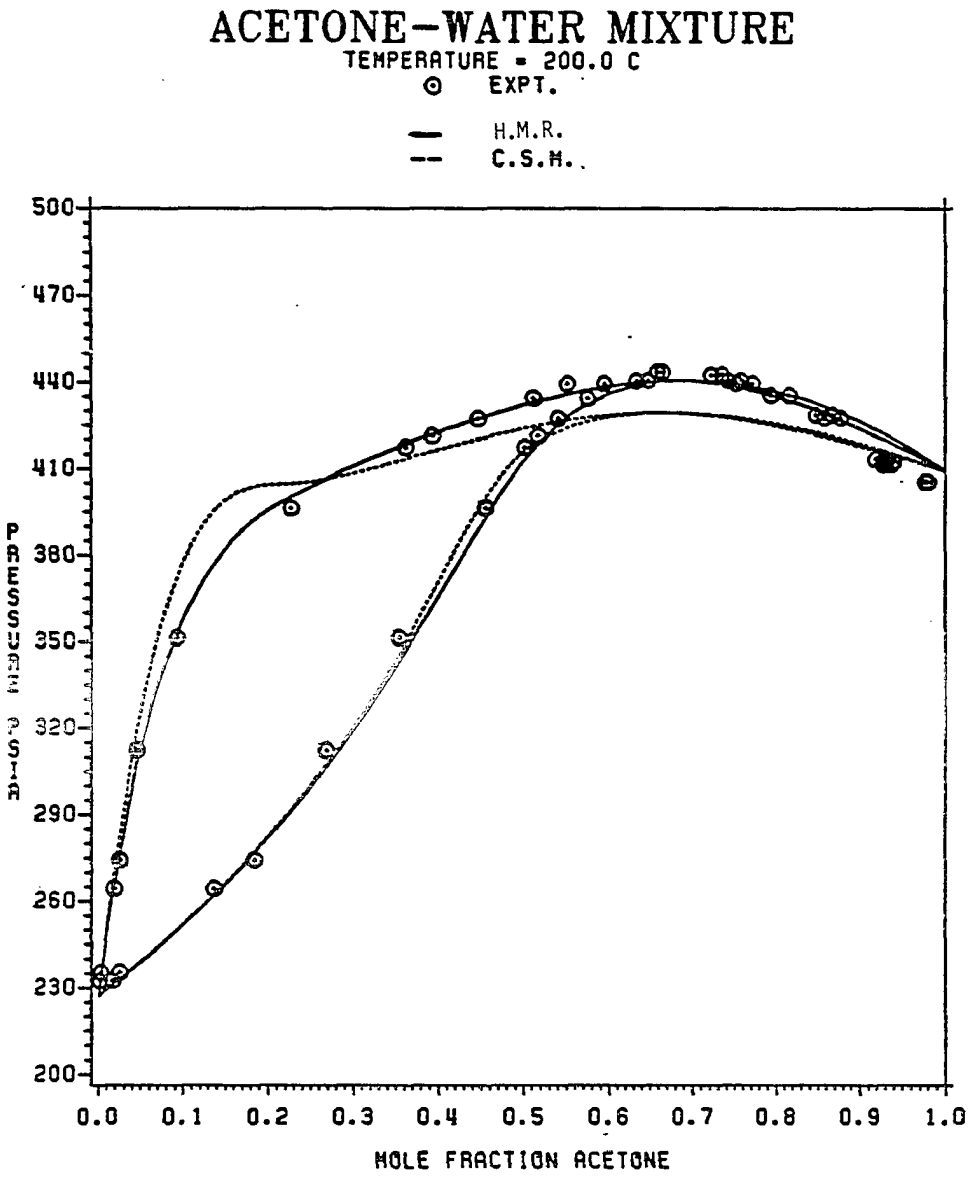
THE P-X DIAGRAM OF THE ACETONE-WATER SYSTEM AT 100.0 C

FIGURE 15



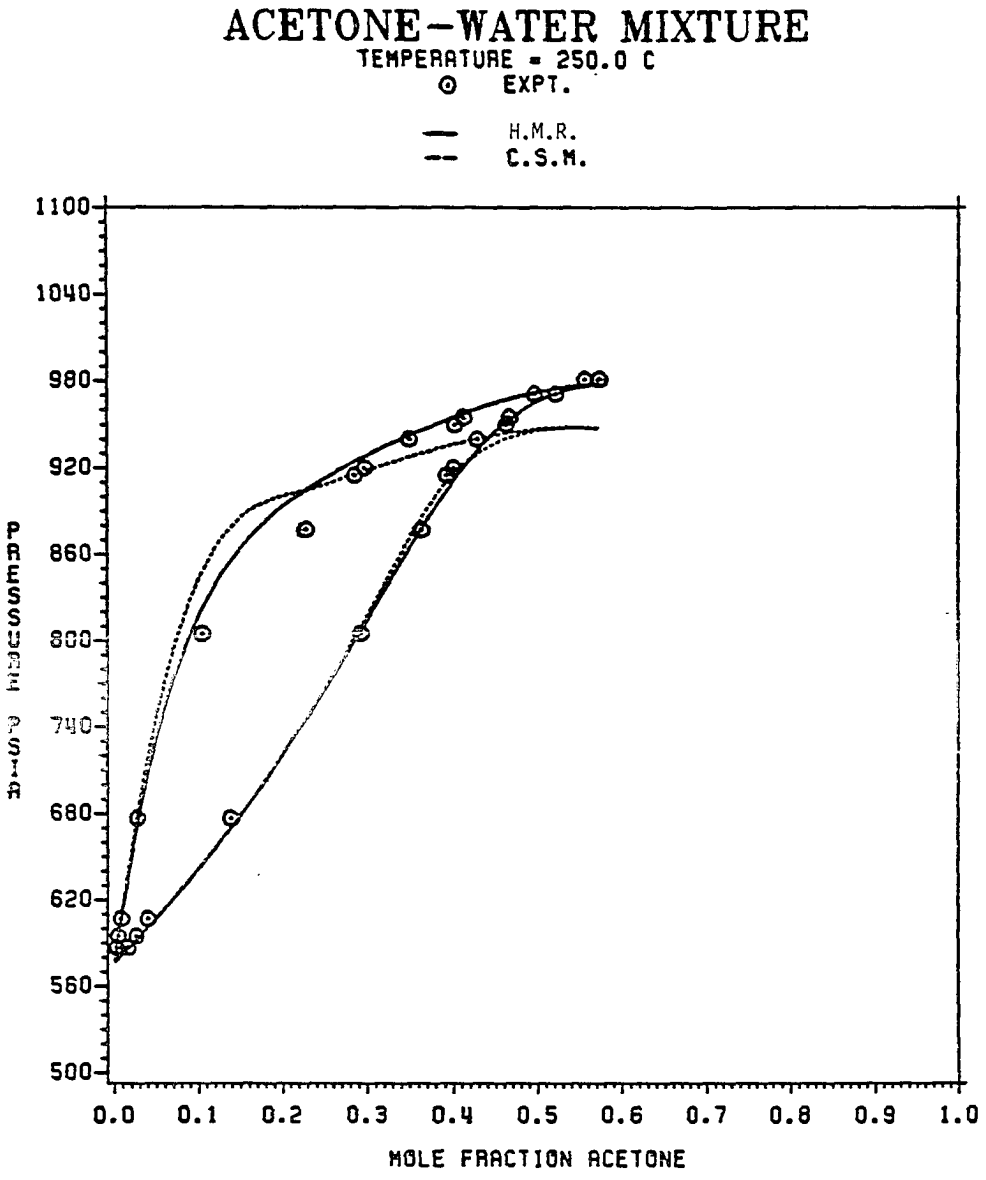
THE P-X DIAGRAM OF THE ACETONE-WATER SYSTEM AT 150.0 C

FIGURE 16



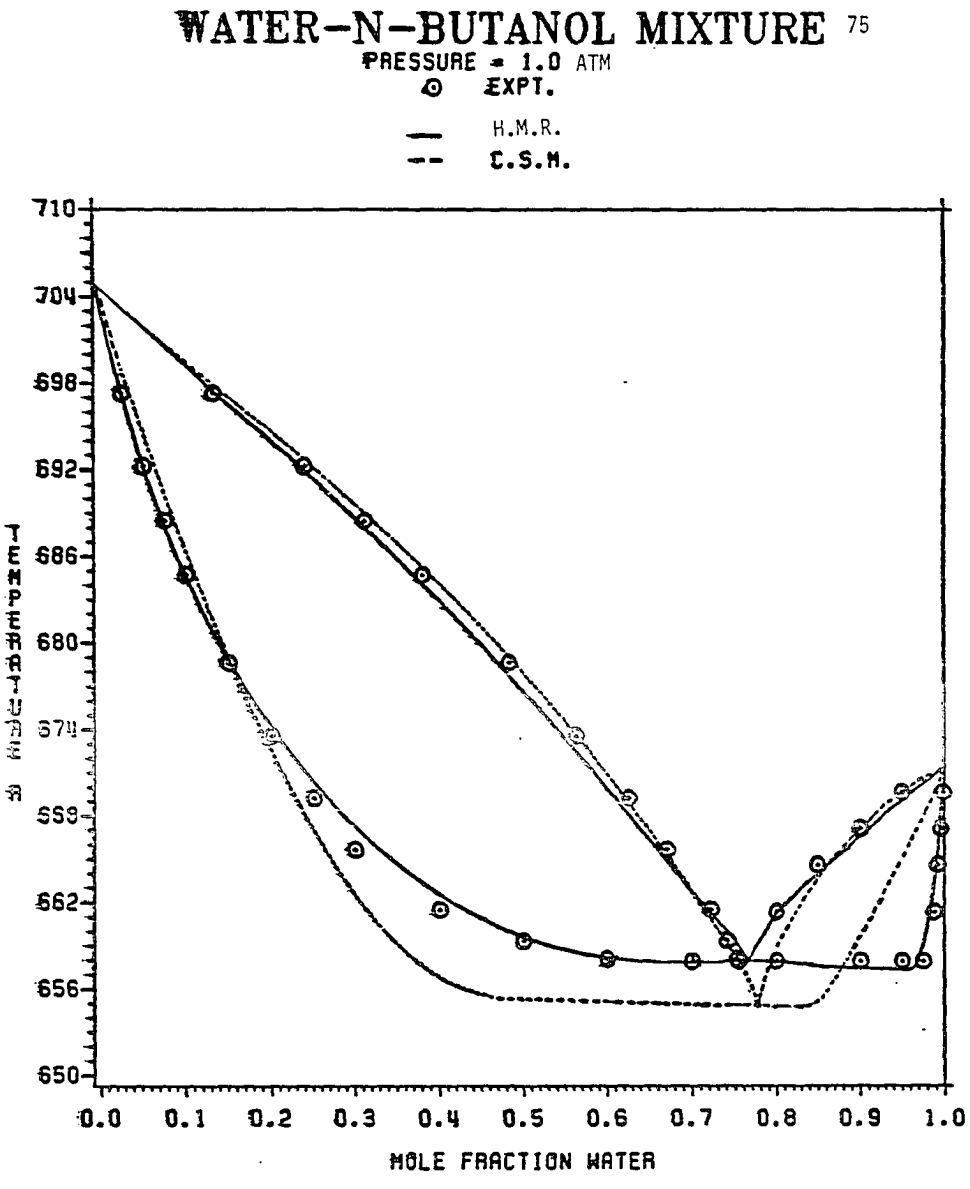
THE P-X DIAGRAM OF THE ACETONE-WATER SYSTEM AT 200.0 C

FIGURE 17



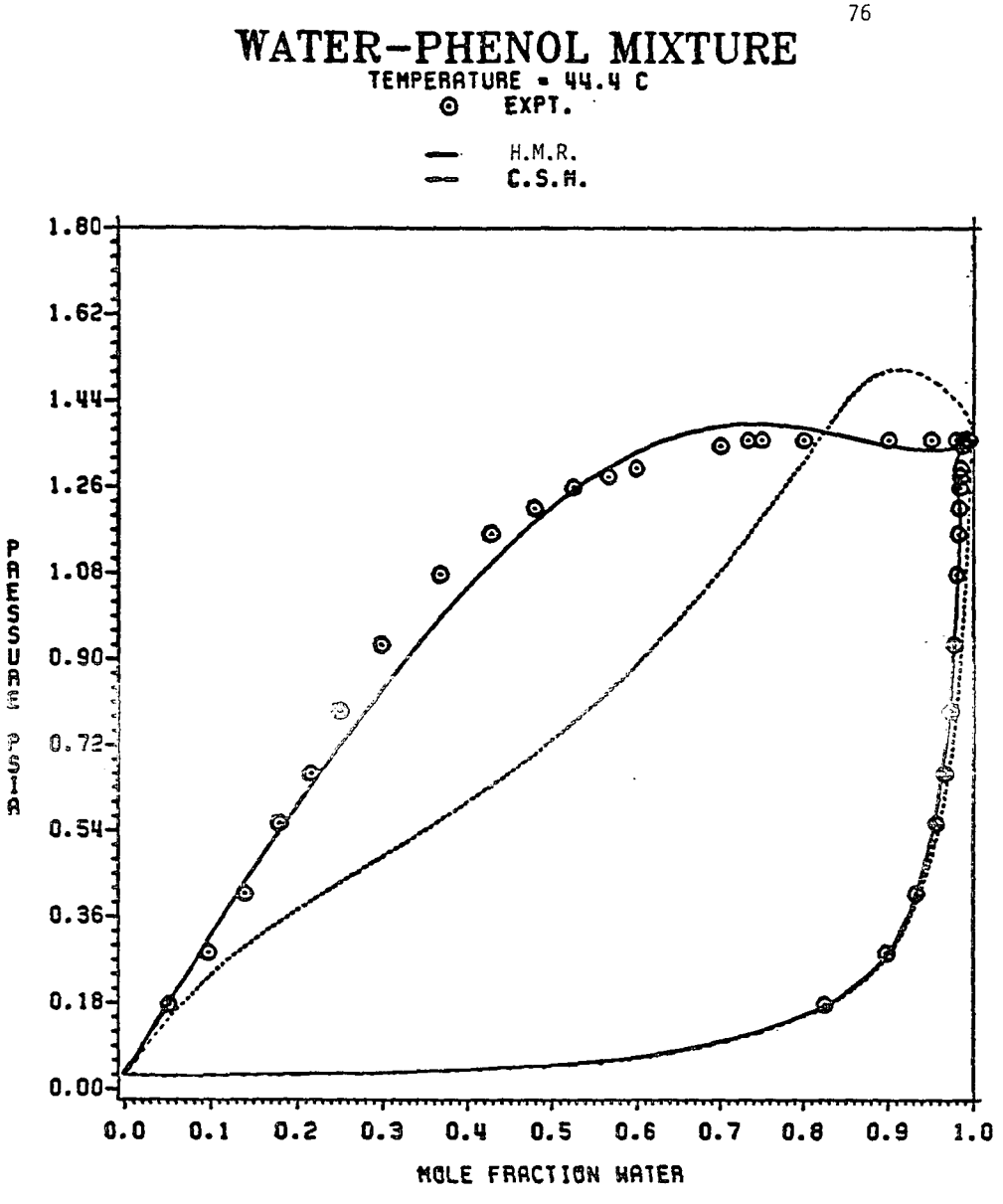
THE P-X DIAGRAM OF THE ACETONE-WATER SYSTEM AT 250.0 C

FIGURE 18



THE T-X DIAGRAM OF THE WATER-N-BUTANOL SYSTEM
AT ATMOSPHERIC PRESSURE

FIGURE 19



THE P-X DIAGRAM OF THE WATER-PHENOL SYSTEM AT 44.4 C

FIGURE 20

For the polar-polar binary systems, again the HMR is able to describe phase behavior with reasonable accuracy.

6.3 Application to Nonpolar-Nonpolar Binary Systems.

The applicability of the HMR was also tested for nonpolar-nonpolar systems. Table VI.9 lists these systems. The binary parameters are given in table VI.10 together with the results for K value predictions. For the nonpolar mixtures of nearly equal size molecules such as cyclohexane-toluene, ethane-n-butane and propane-n-butane, the CSM and the HMR (with $\Delta_{12} = \Delta_{21} = 0$) give good results. For mixtures of differently sized molecules, the HMR with two binary parameters was totally inadequate. Three parameters were needed to adequately correlate the data. The CSM can adequately represent these systems using only two binary parameters. The CSM is applicable to nonpolar mixtures regardless of mixture component molecular size.

The HMR is adequate for nonpolar mixtures but that HMR with $\Delta_{ij} = 0$ is not adequate for mixtures of systems with greatly differing molecular sizes.

Table VI.9

Temperature and Pressure Ranges, and Data References for the Nonpolar - Nonpolar Binary Systems Studied in This Work.

Systems (1) - (2)	Pro.	No. of points	T range K	P range atm	Data References
Benzene-Cyclohexane	VLE	22	298-352	0.12-1.00	Donald et al. 1958 Tasic et al. 1978
Benzene-Hexane	VLE	23	298-328	0.15-0.63	Smith et al. 1970 Yuan et al. 1963
Cyclohexane-Toluene	VLE	31	354-381	1	Myers 1956
Methylcyclohexane-Toluene	VLE	31	333-373	0.19-1.00	Schneider 1961
Ethane-n-Butane	VLE	19	192-199	3-50	Wichterle et al. 1970
Propane-n-Butane	VLE	17	362-392	20-37	Kay 1970
Methane-Ethane	VLE	42	338-393	34-54	Mehra et al. 1965
Methane-Tetralin	VLE	14	543-665	30-223	Sebastian et al. 1979
Methane-n-Decane	VLE	11	543-583	50-125	Lin et al. 1979
Methane-n-Hexadecane	VLE	10	543-704	30-200	Lin et al. 1980
Hydrogen-Propane	VLE	16	298-348	34-204	Trust and Kurata 1971
Hydrogen-n-Butane	VLE	60	338-394	11-170	Klink et al. 1975

Table VI.10

Results of Vapor-Liquid Equilibrium Predictions, and
Binary Interaction Parameters for NonPolar-NonPolar Binary Systems

Systems (1) - (2)	Model	ξ_{ij}	ζ_{ij}	Δ_{ij} (cal/gmol)	Δ_{ji} (cal/gmol)	% AARD K 1	% AARD K 2
Benzene-Hexane	H.M.R.	0.9800	0.9692	0.0	0.0	3.70	3.12
	C.S.M.	0.9787	0.9817	-	-	3.54	3.07
Benzene-Cyclohexane	H.M.R.	0.9414	0.9953	0.0	0.0	0.98	1.53
	C.S.M.	0.9459	0.9947	-	-	0.90	1.57
Cyclohexane-Toluene	H.M.R.	0.9349	1.0084	0.0	0.0	0.76	2.07
	C.S.M.	0.9877	0.9910	-	-	0.69	1.80
Methyl cyclohexane-Toluene	H.M.R.	1.0190	0.9848	0.0	0.0	1.53	2.13
	C.S.M.	1.0079	0.9906	-	-	1.09	2.22
Propane-n-Butane	H.M.R.	0.9704	1.0111	0.0	0.0	1.45	1.14
	C.S.M.	1.0019	0.9869	-	-	1.92	2.50
Ethane-n-Butane	H.M.R.	0.9818	0.9800	0.0	0.0	1.26	1.98
	C.S.M.	0.9989	0.9494	-	-	2.88	3.12
Methane-Ethane	H.M.R.	1.0105	1.0479	0.0	0.0	0.89	5.57
	C.S.M.	1.0054	0.9792	-	-	0.98	5.09

Table VI.10 (Continued)

Systems (1) - (2)	Model	ξ_{ij}	ζ_{ij}	Δ_{ij} (cal/gmol)	Δ_{ji} (cal/gmol)	% AARD K 1	% AARD K 2
Methane-Tetralin	H.M.R.	1.0181	0.8168	0.0	0.0	20.00	19.12
	H.M.R.	1.1825	1.0000	-1374.26	1956.37	7.75	9.80
	C.S.M.	1.0778	0.8168	-	-	6.50	8.50
Methane-n-Decane	H.M.R.	1.2622	1.3947	0.0	0.0	17.24	19.24
	H.M.R.	1.1531	1.0000	-1953.23	19132.96	2.61	7.38
	C.S.M.	1.1078	0.8540	-	-	2.31	4.85
Methane-n-Hexadecane	H.M.R.	1.1460	1.8050	0.0	0.0	26.53	50.60
	H.M.R.	1.0000	1.5497	-1214.69	90.73	12.50	13.70
	C.S.M.	1.1323	0.7618	-	-	7.72	9.63
Hydrogen-Propane	H.M.R.	1.1040	1.5800	0.0	0.0	10.97	15.43
	H.M.R.	1.1222	1.0000	-8130.78	3404.01	6.13	7.89
	C.S.M.	1.0773	1.2863	-	-	7.14	12.60
Hydrogen-n-Butane	H.M.R.	1.1550	1.6650	0.0	0.0	10.67	17.30
	H.M.R.	1.1600	1.0000	-2762.00	16473.00	2.89	12.30
	C.S.M.	1.1029	1.3286	-	-	4.83	13.81

CHAPTER VII

PREDICTIONS OF THERMODYNAMIC PROPERTIES FOR MULTICOMPONENT MIXTURES

This section illustrates the extension of the HMR to multicomponent systems by considering n different types of cells in the fluid, where n is the total number of components in the fluid mixture. A molecule of type i is at the center of each cell (i=1,2,.... n). Four ternary mixtures were studied each consisting of two hydrocarbons (cyclohexane, benzene, n-hexane, toluene and methylcyclohexane) and one polar and associating compound (aniline, ethanol). The list of systems are presented in table VII.1, together with the ranges of the data used and the data references. Predictions of VLE behavior for each system were achieved by performing isothermal flash calculations. The parameters for each of the pairs of components were those determined from fitting the binary VLE data. These binary parameters were reported in table VI.4 and VI.10. No ternary parameters were required. The results are given in table VII.2. Generally, the HMR yields better results than the CSM. The CSM predicted K- values and

Table VII.1

Temperature and Pressure Ranges, and Data References for the Ternary Systems Studied in This Work.

Systems (1) -- (2) -- (3)	Pro.	No. of points	T range K	P range atm	Data References
Cyclohexane-Aniline-Benzene	VLE	10	343	0.34-0.69	Podder 1963
Methylcyclohexane-Aniline-Toluene	VLE	25	353-373	0.32-0.90	Schneider 1961
n-Hexane-Ethanol-Benzene	VLE	42	328	0.54-0.88	Yuan et al. 1963
Toluene-Cyclohexane-Ethanol	VLE	10	323	0.32-0.50	Zharov et al. 1968

Table VII.2

Results of Vapor-Liquid Equilibrium Predictions for Ternary Systems

Systems (1) - (2) - (3)	Model	% AARD								
		K 1	K 2	K 3	X 1	X 2	X 3	Y 1	Y 2	Y 3
Cyclohexane-Aniline-Benzene	H.M.R.	2.65	2.35	2.93	2.77	4.01	2.91	0.14	4.91	0.17
	C.S.M.	12.61	4.28	8.24	16.00	13.93	9.24	0.37	16.12	0.44
Methyl cyclohexane-Aniline-Toluene	H.M.R.	3.61	7.62	2.08	3.79	6.91	2.02	0.18	2.96	0.15
	C.S.M.	6.94	6.59	2.88	8.42	13.85	2.36	0.83	11.46	0.99
n-Hexane-Ethanol-Benzene	H.M.R.	7.88	10.32	7.79	8.81	10.74	7.07	8.31	4.59	5.19
	C.S.M.	41.00	35.24	21.98	21.54	49.27	19.41	9.44	15.85	7.3
Toluene-Cyclohexane-Ethanol	H.M.R.	6.17	8.37	12.02	10.60	11.91	17.78	11.36	3.15	2.58
	C.S.M.	14.94	29.25	33.77	21.52	47.45	43.61	26.33	2.00	9.65

phase compositions for cyclohexane-aniline-benzene and methylcyclohexane-aniline-toluene systems with reasonable accuracy. However, results were not as good for the mixtures containing ethanol. This decrease in accuracy is probably due to the difference in size, shape and polarity between ethanol and aniline molecules. However, the results generally indicate reliable predictions of VLE for multicomponent systems using the HMR.

CHAPTER VIII

COMPOSITION DEPENDENCE OF THE EXCESS GIBBS FREE ENERGY

From an equation of state, the fugacity coefficient of component i in the mixture Φ_i, and in the pure state Φ_i^* at the same temperature and pressure as the mixture can be calculated (see appendix A and B). The activity coefficient of component i in the mixture can be defined as:

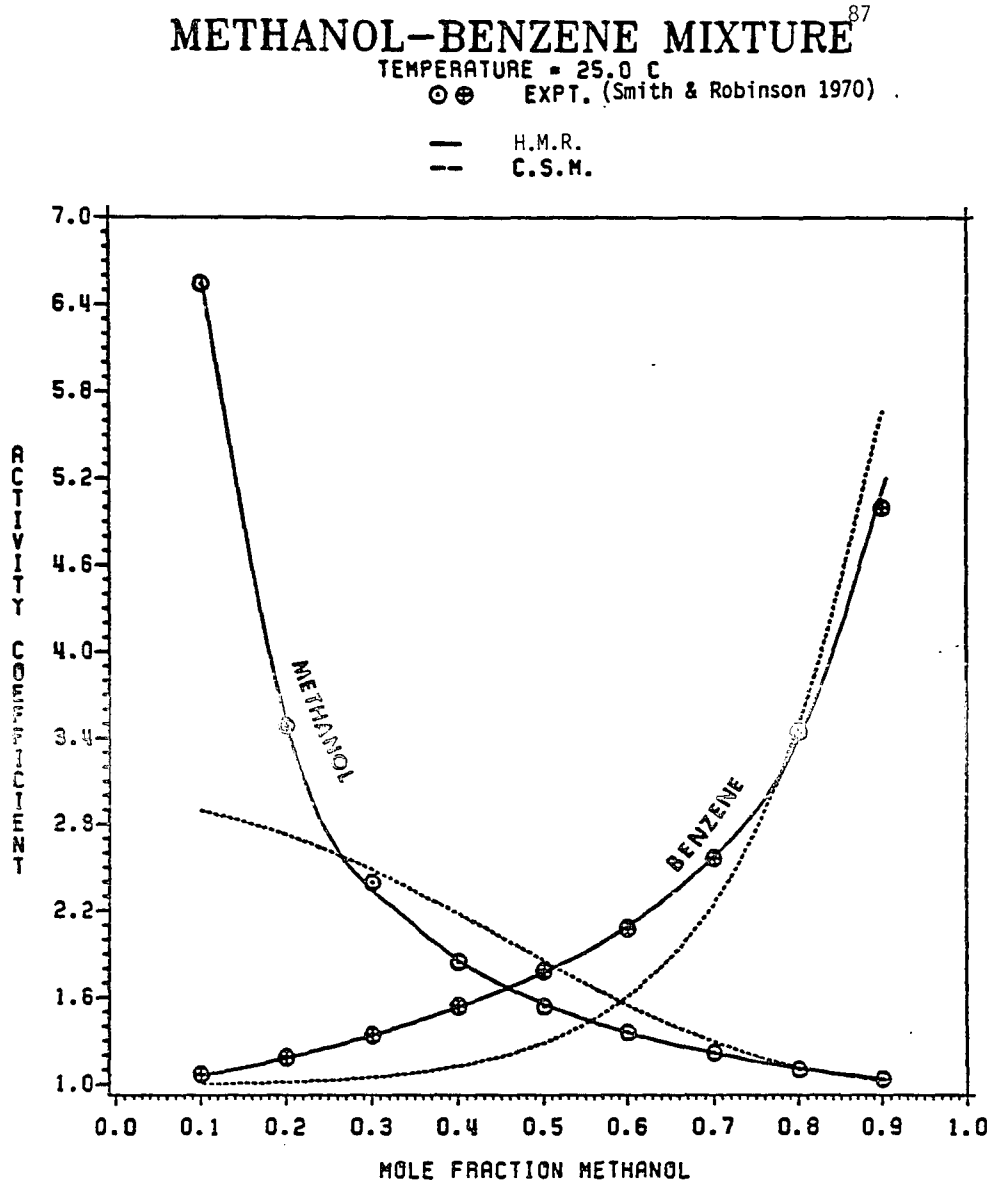
$$\Gamma_i = \frac{\Phi_i}{\Phi_i^*} \qquad (55)$$

and the excess Gibbs free energy can be expressed as:

$$G^E = RT \sum_i x_i \ln \Gamma_i \qquad (56)$$

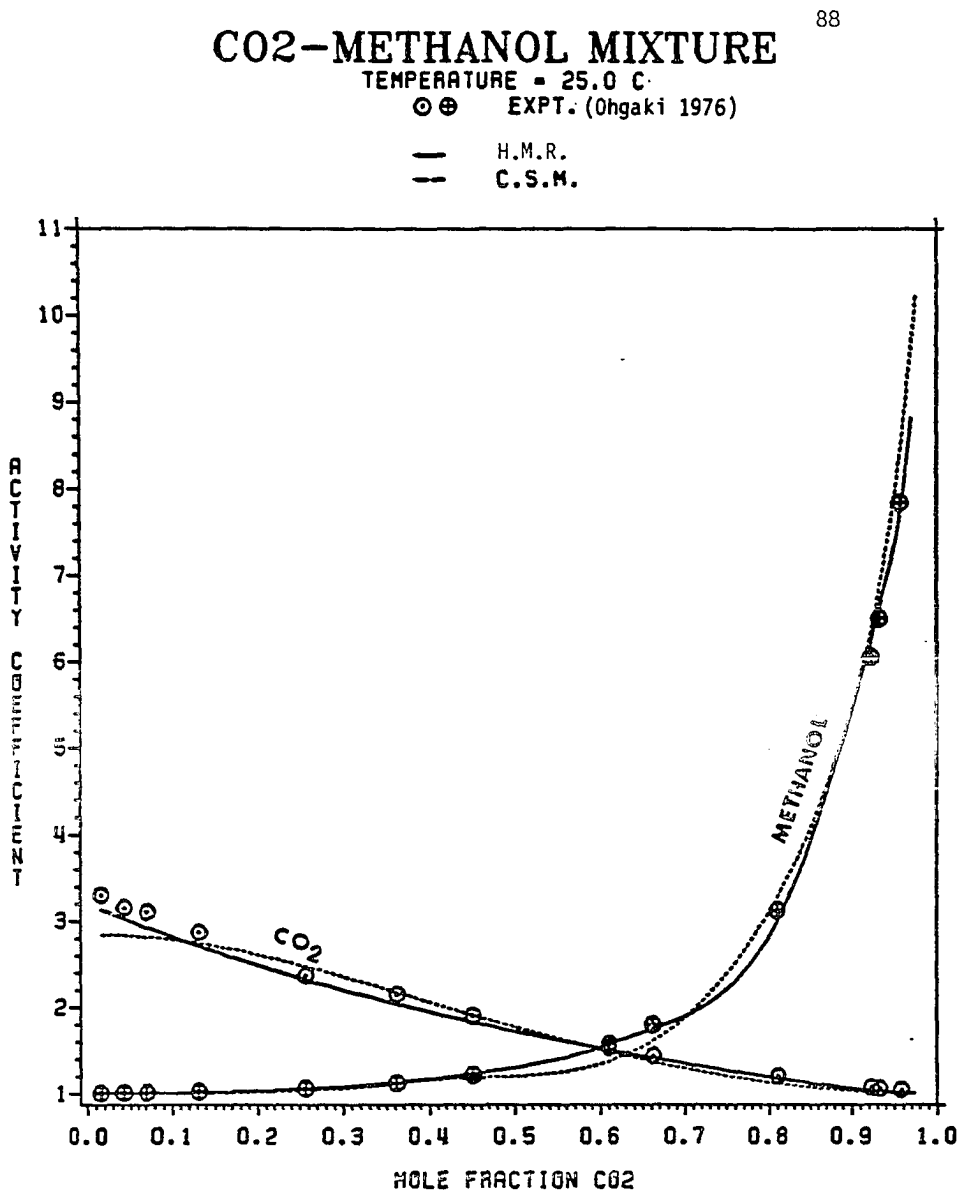
The excess properties, for example the excess Gibbs free energy, although important, are often not used in the development of theories and physical properties correlations describing gas and liquid behavior, since PVT and VLE data usually are sufficient. When the excess Gibbs free energy

and/or activity coefficient data are not included in determining the binary parameters, the calculated fugacity coefficients may differ from experiment, even though the calculated fugacity coefficients in the liquid phase are the same as those in the vapor phase. Figures 21-23 show comparisons of experimental and calculated activity coefficients for some selected binary systems. Figures 24-26 show the composition dependence of the excess Gibbs free energy. For highly nonideal solutions such as methanol-benzene mixture, the activity coefficients at the dilute compositions are substantially different from unity (see Figure 21). The HMR is able to reproduce the data while the CSM fail badly. These effects are reflected in the excess Gibbs free energy predictions (see Figure 24). When the activity coefficients approach unity, the difference between these calculations are essentially indistinguishable. Figures 21-23 indicate the VLE calculations in this work using the HMR did not falsify the activity coefficients and Figures 24-26 show good predictions of excess Gibbs free energy for the total composition range using the HMR, without including these data in the fit. The prediction accuracy for VLE is commensurate with that obtained for excess Gibbs free energy.



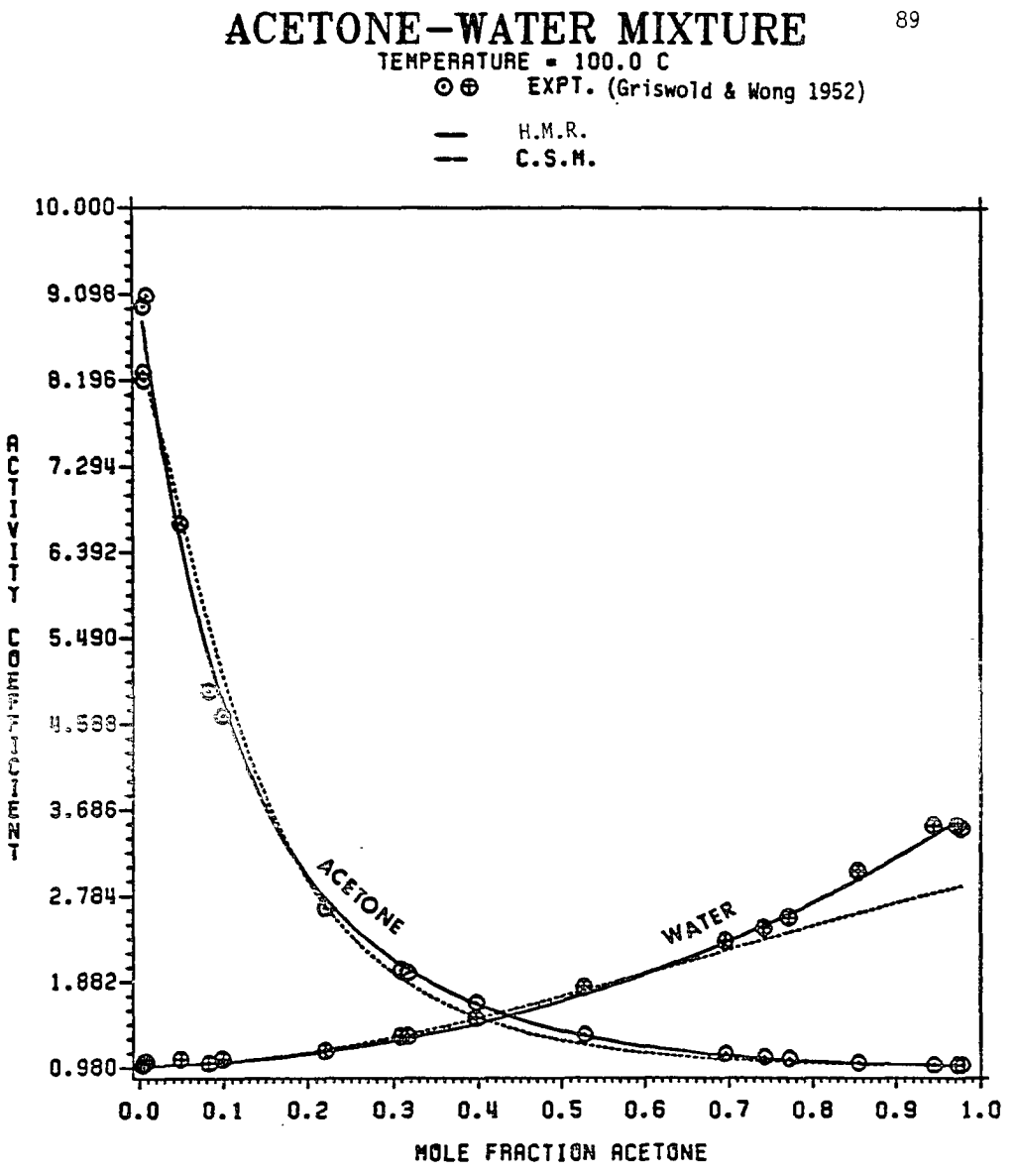
ACTIVITY COEFFICIENTS OF THE METHANOL-BENZENE SYSTEM AT 25.0 C

FIGURE 21



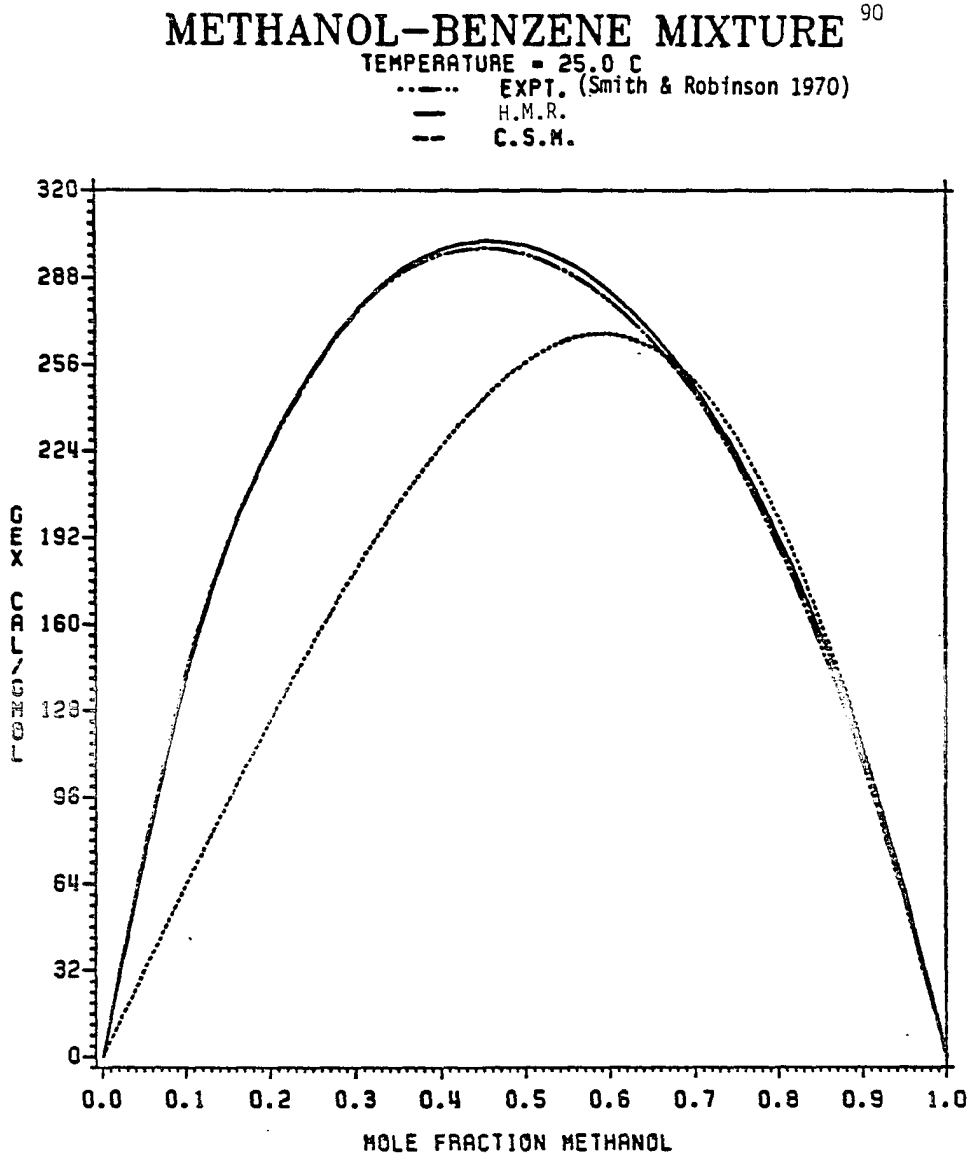
ACTIVITY COEFFICIENTS OF THE CO2-METHANOL SYSTEM AT 25.0 C

FIGURE 22



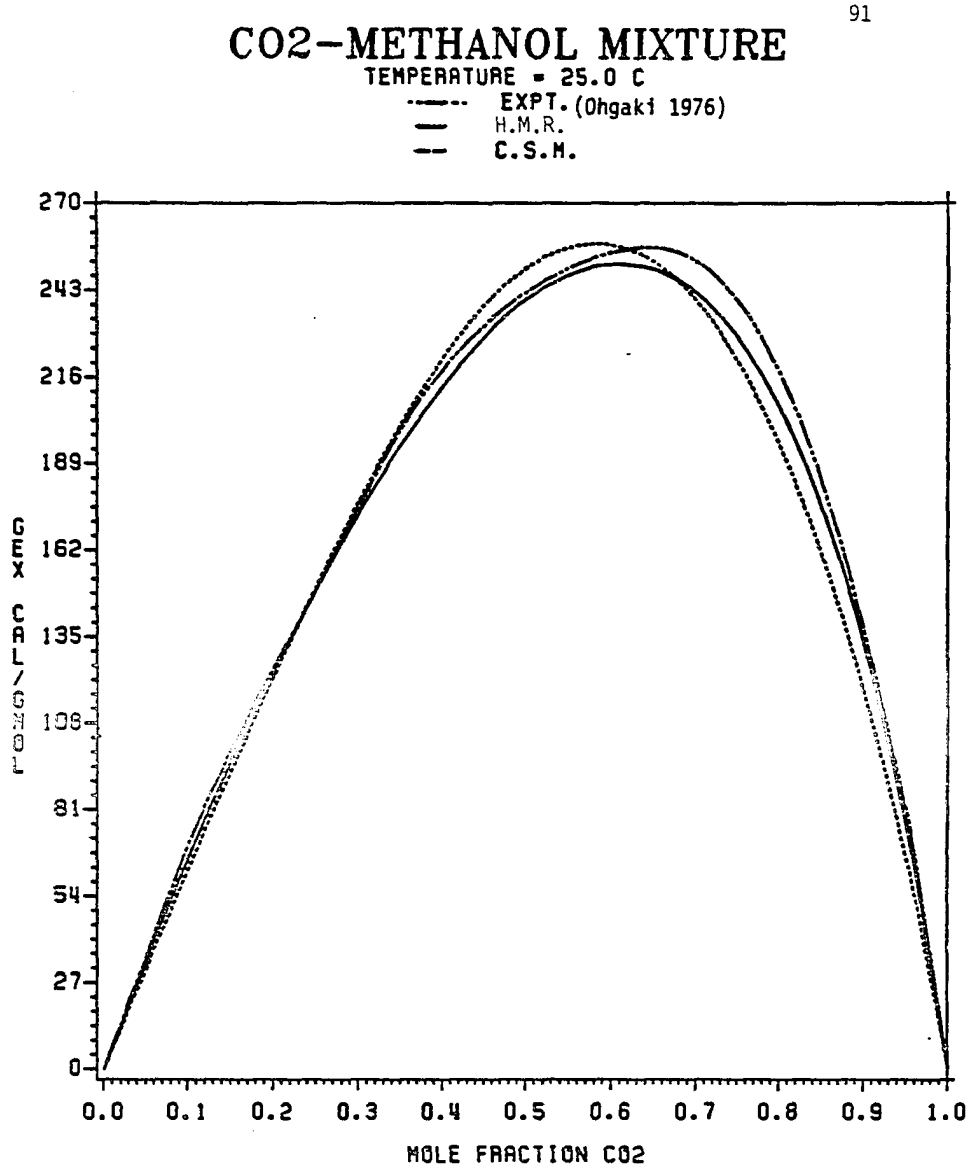
ACTIVITY COEFFICIENTS OF THE ACETONE-WATER SYSTEM AT 100.0 C

FIGURE 23



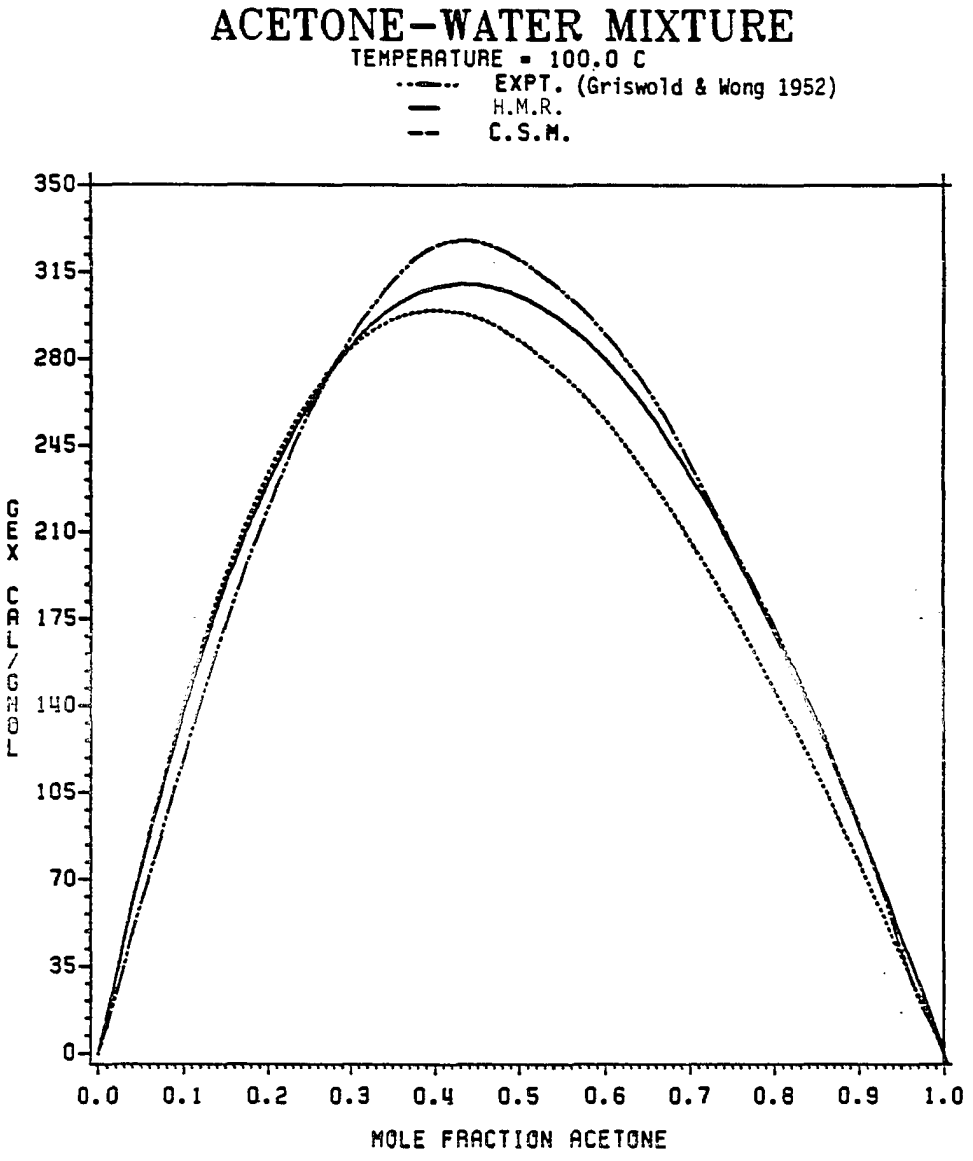
EXCESS GIBBS ENERGY FOR THE METHANOL-BENZENE SYSTEM AT 25.0 C

FIGURE 24



EXCESS GIBBS ENERGY FOR THE CO2-METHANOL SYSTEM AT 25.0 C

FIGURE 25



EXCESS GIBBS ENERGY FOR THE ACETONE-WATER SYSTEM
AT 100.0 C

FIGURE 26

CHAPTER IX

PREDICTIONS OF LIQUID-LIQUID EQUILIBRIA

A water-rich liquid phase will form when the water present in a hydrocarbon mixture exceeds its solubility limit. The presence of this free-water phase in the process stream poses adverse effects such as corrosion. Therefore, the knowledge of hydrocarbon-water mutual solubility is very important in the petroleum, synthetic fuels, chemical and petrochemical industries. To provide further perspective of the applicability of the HMR, it was tested using liquid-liquid equilibria (LLE) data for coal fluid-water systems. Table IX.1 lists seven representative model coal compound+water binary mixtures. Generally, LLE is very difficult to describe. This difficulty is due to the differences in the solubilities of hydrocarbons and water in two liquid phases. The water-rich phase is almost pure water, and the hydrocarbon-rich liquid phase can contain a significant amount of water. Four parameters were fit to the HMR, and two parameters were fit to the CSM. Several attempts were made to add more parameters to the CSM, but the physical meaning of the obtained binary parameters was

Table IX.1

Temperature and Pressure Ranges, and Data References for the Coal Fluid - Water Binary Systems Studied in This Work.

Systems (1) -- (2)	Pro.	No. of points	T range K	P range atm	Data References
Benzene--Water	LLE	6	313-473	0.3-30.20	Tsonopoulos et al. 1982
Cyclohexane-Water	LLE	8	313-482	0.3-30.00	Tsonopoulos et al. 1982
Hexane-water	LLE	6	310-473	0.45-35.1	Tsonopoulos et al 1982
Ethylbenzene-Water	LLE	6	373-804	1.0-85.0	Brady et al. 1982
Ethylcyclohexane-Water	LLE	6	373-804	1.0-87.0	Brady et al. 1982
1-Methylnapthalene-Water	LLE	6	373-804	2.0-63.2	Brady et al. 1982
1-Ethylnapthalene-Water	LLE	6	373-804	2.0-63.0	Brady et al. 1982

[1] LLE = Liquid-Liquid Equilibrium

lost, and the prediction results were not satisfactory. The binary parameters are reported in table IX.2. Results are given in table IX.3 in terms of average absolute relative deviation for predicted mole fractions. Significant improvements over the CSM were obtained using the HMR. Figures 27-30 show the experimental and calculated LLE for four selected systems. The CSM is not able to predict LLE, while the HMR is adequate for LLE calculations.

Table IX.2

Binary Interaction Parameters for
Coal Fluid-Water Systems
(Liquid-Liquid Equilibrium)

Systems (1) - (2)	Model	ξ_{ij}	ζ_{ij}	Δ_{12} (cal/gmol)	Δ_{21} (cal/gmol)
Benzene-Water	H.M.R.	0.6938	0.7239	4431.71	176.52
	C.S.H.	0.5578	0.1310	-	-
Cyclohexane-Water	H.M.R.	0.3158	0.6190	-34.00	7541.40
	C.S.H.	0.5943	0.1568	-	-
Hexane-Water	H.M.R.	0.1000	0.6224	7768.46	4.12
	C.S.H.	0.5712	0.1423	-	-
Ethybenzene-Water	H.M.R.	0.2341	0.6878	5040.95	418.86
	C.S.H.	0.5319	0.4679	-	-
Ethylcyclohexane-Water	H.M.R.	0.1000	0.5763	7476.78	155.24
	C.S.H.	0.5629	0.1137	-	-
1-Methylnapthalene-Water	H.M.R.	0.2682	0.9088	-258.19	-2459.91
	C.S.H.	1.3601	0.9167	-	-
1-Ethylnapthalene-Water	H.M.R.	0.2000	0.9085	-270.95	-2829.23
	C.S.H.	1.1273	0.8565	-	-

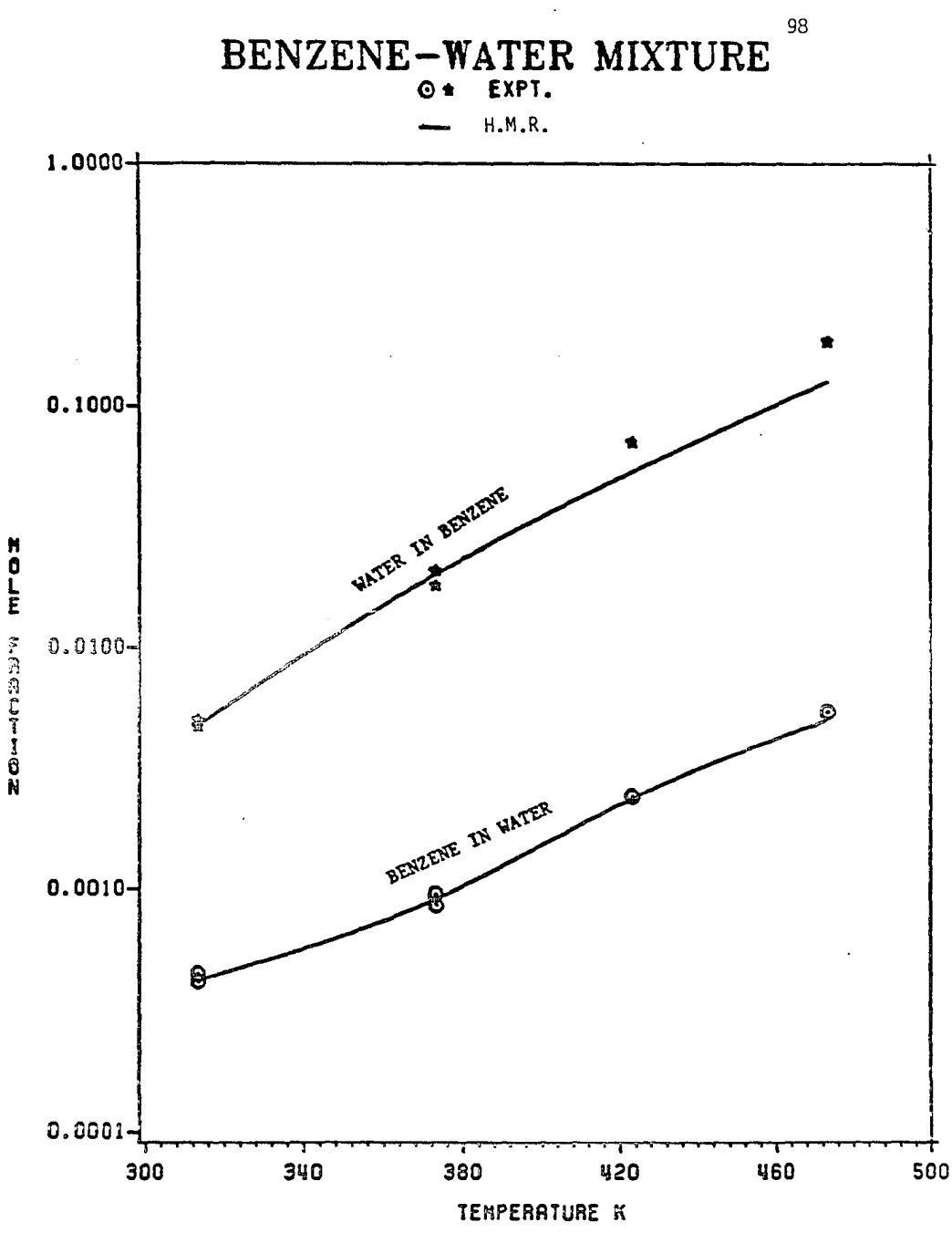
Table IX.3

Results of Liquid-Liquid Equilibrium Predictions
for Coal Fluid-Water Systems

Systems (1) - (2)	Model	% AARD $x_1^{\$}$	% AARD x_2^{ε}
Benzene-Water	H.M.R.	3.86	12.93
	C.S.H.	50.46	337.12
Cyclohexane-Water	H.M.R.	11.46	18.59
	C.S.H.	173.00	1431.66
Hexane-Water	H.M.R.	11.37	14.79
	C.S.H.	2137.44	1139.23
Ethybenzene-Water	H.M.R.	24.68	14.07
	C.S.H.	777.25	1015.66
Ethylcyclohexane-Water	H.M.R.	27.58	28.36
	C.S.H.	116.31	3361.88
1-Methylnapthalene-Water	H.M.R.	29.54	14.74
	C.S.H.	6870.10	3899.06
1-Ethylnapthalene-Water	H.M.R.	27.77	12.33
	C.S.H.	5949.70	3833.06

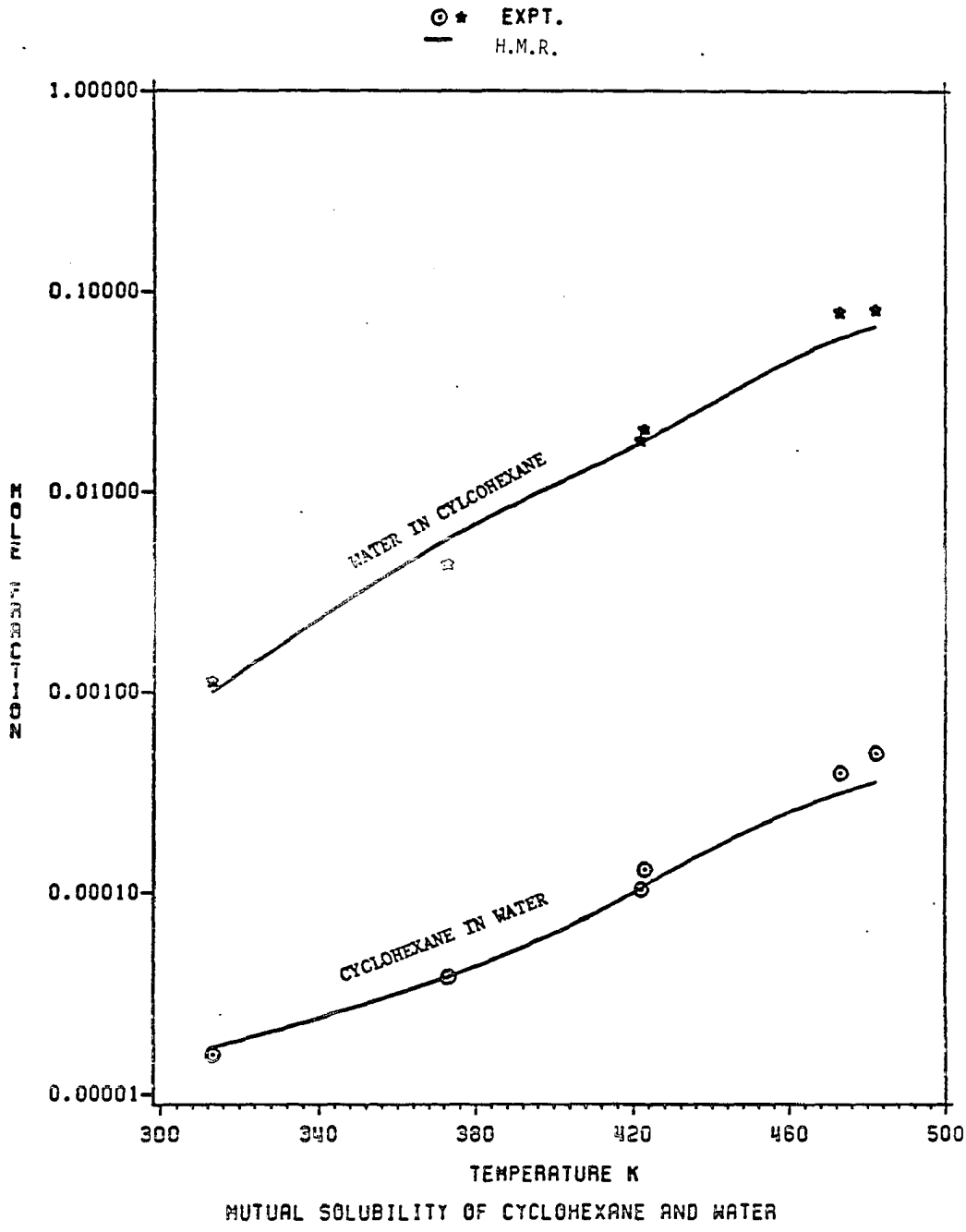
$ Mole fraction of component 1 in liquid phase 2

ε Mole fraction of component 2 in liquid phase 1



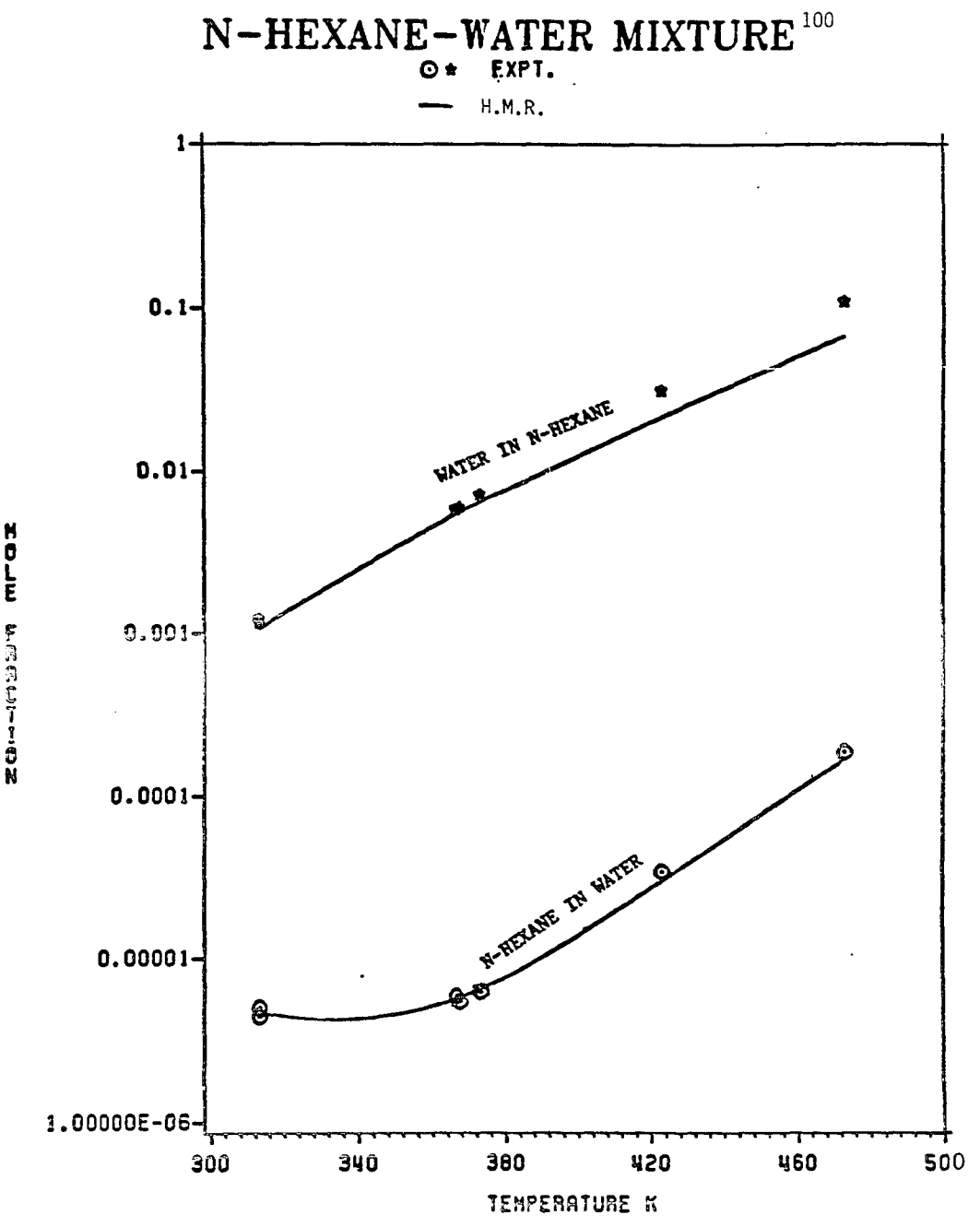
MUTUAL SOLUBILITY OF BENZENE AND WATER

FIGURE 27



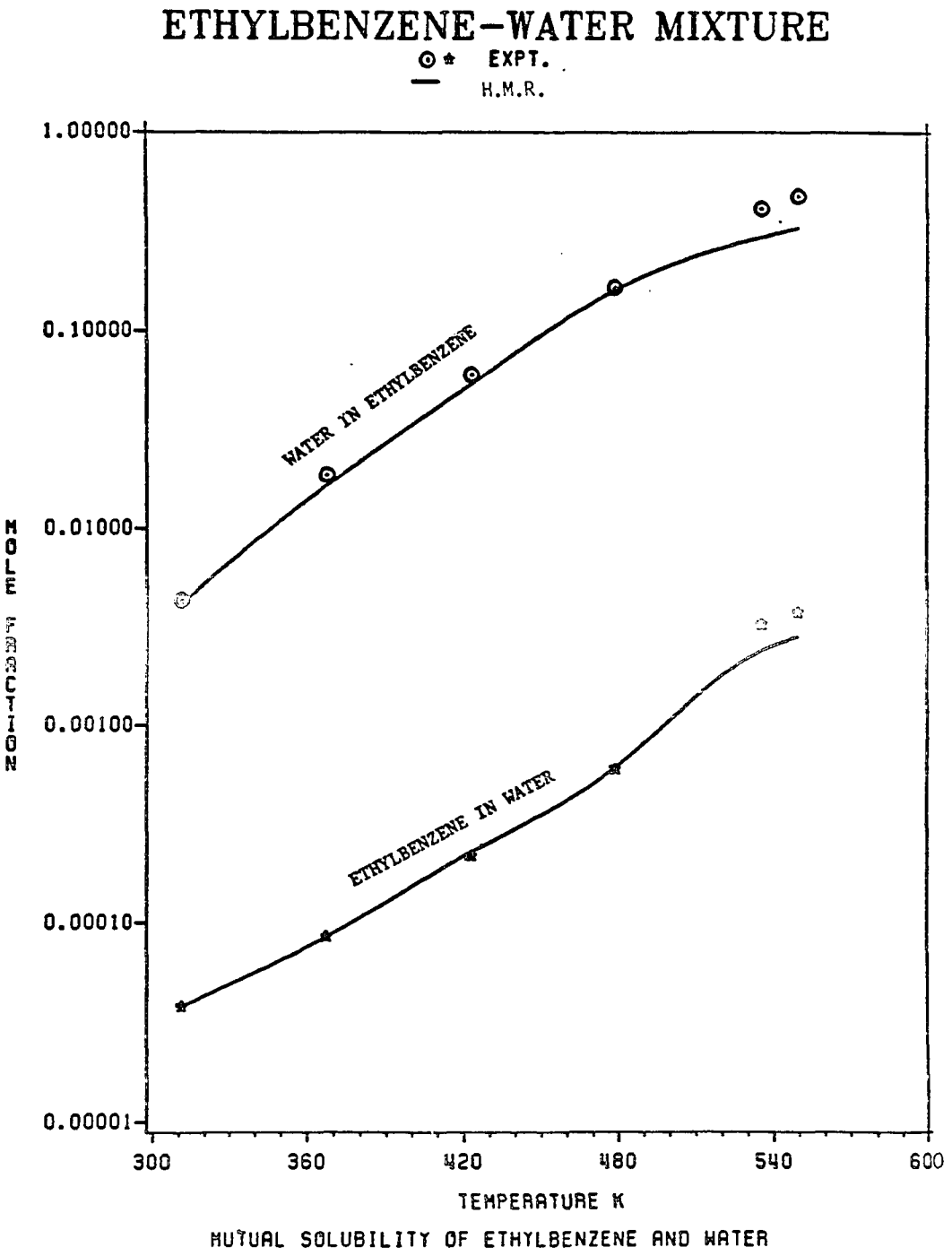
MUTUAL SOLUBILITY OF CYCLOHEXANE AND WATER

FIGURE 28



MUTUAL SOLUBILITY OF N-HEXANE AND WATER

FIGURE 29



MUTUAL SOLUBILITY OF ETHYLBENZENE AND WATER

FIGURE 30

CHAPTER X

CONCLUSIONS AND RECOMMENDATIONS

The local composition model was used to develop a mixing rule for the characteristic energy parameter ε_x in the MPM correlation. The mixing rules for the size parameter σ_x^3 and the orientation parameter γ_x were based on the conventional one-fluid model. Consequently, the mixing rules for the MPM correlation contain characteristics of both one and two-fluid models. These hybrid mixing rules with the MPM correlation were successfully applied to predict vapor-liquid equilibria and mixture density for binary mixtures of components differing significantly in size, shape, structure and polarity.

Nonpolar-polar binary systems including hydrocarbons with ketones, aniline, alcohols, water and polar-polar binaries such as acetone-water, carbon dioxide-water and water-phenol were well represented by these hybrid mixing rules. On the contrary, the conformal solution model was not able to accurately describe the phase behavior of these highly nonideal solutions. For slightly nonideal solutions such as propane- n-butane, cyclohexane-toluene, both types

of mixing rules gave good VLE predictions. The hybrid mixing rules were also extended to multicomponent systems without requiring additional parameters. These hybrid mixing rules with the parameters obtained from the binaries were tested for VLE calculations for ternary systems such as cyclohexane-aniline-benzene and n-hexane-ethanol-benzene. The prediction accuracy for these ternary systems is commensurate with that obtained for the binaries. The hybrid mixing rules were further applied with satisfactory results to predict liquid-liquid equilibria for coal fluid-water systems such as benzene-water, 1-methylnapthalene-water and ethylbenzene-water. The conformal solution model could not predict liquid-liquid equilibria behavior accurately.

The calculated activity coefficients from the HPN correlation with the hybrid mixing rules were also studied. The excess Gibbs free energy was also predicted with reasonable accuracy by the hybrid mixing rules.

A significant point in this study is that the hybrid mixing rules, which are based on one and two-fluid models can accurately predict fluid-phase equilibria for many types of mixtures corresponding to different types of phase behavior.

In order to be applicable in industry, correlations must be relatively simple and convenient to use. It is recommended that the binary parameters needed in the present correlation be correlated as functions of temperature for mixtures with azeotropic phase behavior and that the

parameters be further generalized so that the hybrid mixing rules may be more conveniently applied to multicomponent mixtures.

NOMENCLATURE

Roman

$A - A^0$	Helmholtz free energy departure
A	Helmholtz free energy
E_i	generalized ith equation-of-state parameter
a_i, b_i	universal constant in expression for E
f_i	fugacity of the ith component in a mixture
f_i^0	standard-state reference fugacity
g_{ij}	radial distribution function
G^E	excess Gibbs free energy
$H - H^0$	enthalpy departure
k	Boltzmann constant (1.38054×10^{-23} J/K)
L_{ij}	nearest neighbor distance
n_{ij}	nearest neighbor number of molecules of type i surrounding the central j molecule
N	total number of molecules
P	absolute pressure
P^0	ideal gas pressure
R	Ideal gas constant
T	absolute temperature
T^*	reduced temperature

Roman

T_c	critical temperature
$S - S^0$	entropy departure
u_{ij}	molar internal energy
U	total internal energy
v	specific volume
V_{ij}	spherical volume
V^0	ideal gas volume
x_{ij}	local mole fraction
x_i	total mole fraction
W_{ij}	mean potential of mean force
z	coordination number
Z	compressibility factor

Greek

α	nonrandomness parameter
γ	molecular orientation parameter
Γ_i	activity coefficient of the ith component in a mixture
ε	characteristic molecular-energy parameter
κ	polar and association parameter
ξ_{ij}, ζ_{ij}, Δ_{12}, Δ_{21}	binary interaction parameters
ρ	density
ρ^*	reduced density
ρ_c	critical density

Greek

σ	characteristic molecular-size parameter
Φ_i	fugacity coefficient of the ith component in a mixture
Φ_i^*	fugacity coefficient of the ith component in a pure state at the same T, and P of the mixture

LITERATURE CITED

Abrams, D.S., and J.M. Prausnitz, AIChE, 21, 116 (1975).

Andon, R.J.L., J.D. Cox, and E.F.G. Herington, Trans. Far. Soc., 53, 410 (1957).

Benedict, M., C.A. Johson, E. Solomon, and L.C. Rubin, Trans. of Amer. Ins. of Chem. Eng., 41, 4 (1945).

Boston, J.F., and H.I. Britt, Comp. Chem. Eng., 2, 109 (1978).

Brady, C.J, and G.M. Wilson, Water-Hydrocarbon Liquid-Liquid-Vapor Equilibrium Measurements to 530 F, Reseach Report, RR-62, Gas Proc. Ass. (1982).

Britt, H.I., and R.H. Luecke, Technometrics, 15, 233 (1973).

Brule, M.R., C.T. Lin, S. Watanasiri, and K.E. Starling, AIChE, 29, 616 (1982).

Culberson, O.L., and J.J. MacKetta Jr., Petro. Trans., AIME, 192, 223 (1951).

Culberson, O.L., and J.J. MacKetta Jr., Petro. Trans., AIME, 189, 319 (1951).

Donald, M.B., and K. Ridgway, Chem. Eng. Sci., 5, 188 (1956).

Donald, M.B., and K. Ridgway, J. App. Chem., 8, 403 (1958).

Fisher, J., and S. Lago, J. Chem. Phys., 78, 5750 (1983).

Gay, L., Chim. Ind., 18, 187 (1927).

Gmehling, J., J. Chem. Eng. Data, 27, 4, 371 (1982).

Gmehling, J., U. Onken, and H.W. Schulte, J. Chem. Eng. Data, 25, 1, 29 (1980).

Gmehling, J., U. Onken, "Vapor-Liquid Equilibrium Data Collection",DECHEMA Chemistry Data Series: Frankfurt,

Vol. I, part1 (1977a).

Gmehling, J., U. Onken, "Vapor-Liquid Equilibrium Data Collection",DECHEMA Chemistry Data Series: Frankfurt, Vol. I, part2a (1977b).

Gmehling, J., U. Onken, W. Arlt, "Vapor-Liquid Equilibrium Data Collection",DECHEMA Chemistry Data Series: Frankfurt, Vol. I, part2b (1977c).

Goin, K.M., "Development of Equation of State for Fluid-Correlation Methodology for Thermodynamic and PVT Properties, Including a Case Study for Water," Ph.D. Thesis, The University of Oklahoma, Norman OK (1978).

Griswold, J., and S.Y. Wong, Chem. Eng. Prog. Sympos. Series, 48, 3, 18 (1952).

Guggenheim, E.A., Proc. R. Soc. (London), Ser. A, 148, 304 (1935).

Guggenheim, E.A., Mixtures, Oxford Univ. Press, London (1952).

Guggenheim, E.A., Applications of Statistical Mechanics, Oxford Univ. Press, London (1966).

Gurukul, M.K.A., and B.N. Raju, J. Chem. Eng. Data, 11, 4, 501 (1966)

Hoeisel, C., Ber. Bunsen. Phys. Chem., 85, 1054 (1981).

Hosseini, S.M., and G. Schneider, Z. fur Phys. Chem. Neue Folge, 36, 137 (1963).

Hu, Y., E.G. Azevedo, and J.M. Prausnitz, The molecular basic for local compositions in liquid mixture model. To be published. (1983).

Huron, M.J., and J. Vidal, Fluid Phase Equil., 3, 255 (1979).

Hwang, S.C., and R.L. Robinson, Jr., J. Chem. Eng. Data, 22, 3, 319 (1977).

Ibl, N.D., G. Daenliker, and G. Trumempler, Helv. Chim. Acta, 37, 1661 (1954).

Katayama, T., K. Ohgaki, G. Maekawa, M. Goto, and T. Nagano, J. Chem. Eng. Japan, 8, 2, 89 (1975).

Kato, M., H. Konishi, and M. Hirata, J. Chem. Eng. Data, 15, 3, 435 (1970).

Kay, W.B., J. Chem. Eng. Data, 15, 1, 48 (1970).

Kemeny, S., and P. Rasmussen, Fluid Phase Equil., 7, 197 (1981).

Kretschmer, C.B., and R. Wiebe, J. Amer. Chem. Soc., 71, 1793 (1949).

Kudryavtseva, L.S., M.P. Susarev, Z. Prikl. Khim., 36, 1471 (1963).

Lee, L.L., T.H. Chung, and K.E. Starling, Fluid Phase Equil., 12, 105 (1983).

Lee, T.J., L.L. Lee, and K.E. Starling, ACS Adv. Chem. Ser., 182, 125 (1979).

Luong, T.H., et al., "Development of a Thermodynamic Properties Correlation Framework for the Coal Conversion Industry. Phase III.", Third Semi-Annual Report, The U.S. Department of Energy, Pittsburgh Energy Technology Center (1983).

Martin, A.R., and C.H. George, J. Chem. Soc. (London), 1413 (1931).

Mathias, P.M., and T.W. Copeman, Extension of the Peng-Robinson equation of state to complex mixtures: evaluation of the various forms of the local composition concept, preprint, private communication (1983).

Mehra, V.S., and T. George, J. Chem. Eng. Dev., 10, 4, 307 (1965).

Mikhail, A.Z., and W.R. Kimel, J. Chem. Eng. Data., 6, 4, 533 (1961).

Myer, H.S., Ind. Eng. Chem., 48, 6, 1104 (1956).

Nagata, I., T. Yamada, K. Goto, and K. Kazuma, J. Chem. Eng. Japan, 8, 71 (1975).

Nakanishi, K., S. Okazaki, K. Ikari, T. Higuchi, and H. Tanaka, J. Chem. Phys., 76, 629 (1982).

Nakanishi, K., and K. Toukubo, J. Chem. Phys., 70, 5848, (1979).

Nitta, T., and T. Katayama, J. Chem. Eng. Japan, 7, 381 (1974).

Novak, J.P., P. Vonka, J. Suska, J. Matous, and J. Pick, Coll. Czech. Chem. Comm., 39, 3593 (1974).

Ohgaki, K., and T.Katayama, J. Chem. Eng. Data., 21, 1, 53 (1976).

Ohgaki, K., F. Sano, and T. Katayama, J. Chem. Eng. Data, 21, 1, 55 (1976).

Olds, R.H., B.H. Sage, W.N. Lacey, Ind. Eng. Chem., 34, 10, 1223 (1942).

Palmer, D.A., and D.B. Smith, Ind. Eng. Chem. Proc. Des. Dev., 11, 114 (1972).

Panayiotou, C., and J.H. Vera, Can. J. Chem. Eng., 59, 501 (1981).

Paulaitis, M.E., Private communication, (1984).

Peng, D.Y., and D.B. Robinson, Ind. Eng. Chem. Fund., 15, 59 (1976).

Polder, C., Z. fur Phys. Chem. Neue Folge, 39, 79 (1963).

Reamer, H.H., R.H. Olds, B.H. Sage, and W.N. Lacey, Ind. Eng. Chem., 35, 7, 790 (1943).

Reed, T.M., and K.E. Gubbins, Applied Statistical Mechanics, McGraw-Hill, New York (1973).

Reid, R.C., J.M. Prausnitz, and T.K. Sherwood, Properties Properties of Gases and Liquids, 3rd Ed., McGraw Hill, New York (1977).

Renon, H., and J.M. Prausnitz, AIChE, 14, 135 (1968).

Scatchard, G., and F.G. Satkiewicz, J. Amer. Chem. Soc., 86, 130 (1964).

Scatchard, G., S.E. Wood, and J.M. Mochel, J. Amer. Chem. Soc., 68, 1957 (1946).

Schneider G., Z. fur Phys. Chem. Neue Folge, 24, 165 (1960).

Schneider G., Z. fur Phys. Chem. Neue Folge, 27, 171 (1961).

Scott, R.L., J. Chem. Phys., 25, 193 (1956).

Selleck, F.T., L.T. Carmichael, and B.H. Sage, Ind. Eng. Chem., 44, 3, 2219 (1952).

Smith, V.C., and R.L. Robinson, Jr., J. Chem. Eng. Data, 15, 3, 391 (1970).

Smith, W.R., Can. J. Chem. Eng., 50, 271 (1972).

Starling, K.E., L.L. Lee, K.C. Mo, C.H. Twu, et al., "Self Consistent Correlation of Thermodynamic and Transport Properties", Final Report GRI/AGA/BR-111-1/77-35, Gas Research Institute and American Gas Association, Arlington, VA (1978).

Starling, K.E., L.L. Lee, et al., "Development of a Thermolynamic Properties Correlation Frame Work For the Coal Conversion Industry", Final Report, The U.S. Department of Energy, Pittsburgh Energy Technology Center (1983).

Strubl, K., V. Svoboda, R. Holub, and J. Pick, Coll. Czech. Comm., 35, 3004 (1970).

Sumer, K.M, and A.R. Thompson, J. Chem. Eng. Data, 12, 4, 489 (1967).

Tasic, A., B. Djordjevic, D. Grozdanic, N. Afgan, and D. Malic, Chem. Eng. Sci., 33, 189 (1978).

Tsonopoulos, C., and G.M. Wilson, High temperature mutual solubilities of hydrocarbons and water. I. benzene, cyclohexane, and n-hexane. AIChE (1982).

Tsuboka, T., and T. Katayama, J. Chem. Eng. Japan, 8, 181 (1975).

Vachhani, N.H., and T.F. Anderson, Mixing rules based on the two-fluid theory for representing highly nonideal systems with an equation of state, preprint, private communication (1982).

Weller, R., H. Schumberth, E. Leibnitz, J. Prakt. Chem, 21, 234 (1963).

Whiting, W.B., and J.M. Prausnitz, Fluid Phase Equil., 9, 119 (1982a).

Whiting, W.B., and J.M. Prausnitz, Ind. Eng. Chem. Fund., (1982b).

Wichterle I., and R. Kobayashi, Nomography, Rice Univ. Houston (1970).

Wilson, G.M., J. Am. Chem. Soc., 86, 127 (1964).

Yoshikawa, Y., A. Takagi, and M. Kato, J. Chem. Eng. Data, 25, 4, 344 (1980).

Yuan, K.S., and B.C.-Y. Lu, part I, J.C.K. Ho, and B.C.-Y. Lu,

part II, A.K. Keshpande and B.C.-Y. Lu, part III, J. Chem. Eng. Data, 8, 4, 549 (1963).

Zharov, V.T., A.G. Morachevsky, L.G. Shapil, and I.A. Buevich, Zh. Prikl. Khim., 41, 2443 (1968).

APPENDIX A

EXPRESSIONS FOR DERIVED THERMODYNAMIC PROPERTIES USING THE CSM

The classical thermodynamic relationships for enthalpy departure and Helmholtz free energy departure are given by:

$$H - H^0 = -RT^2 \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} + RT(Z - 1) \qquad (A-1)$$

and

$$\frac{A - A^0}{RT} = \int_0^\rho (Z - 1) \frac{d\rho}{\rho} - \ln \frac{V}{V^0} \qquad (A-2)$$

Other thermodynamic properties are related to $H - H^0$ and $A - A^0$ through the following relations:

$$S - S^0 = \frac{H - H^0}{T} - \frac{(A - A^0)}{T} - R(Z - 1) \qquad (A-3)$$

$$RT \ln \frac{f_i}{P^0 y_i} = \frac{\partial}{\partial n_i} (A - A^0)\Big|_{T, V, n_{j \neq i}} \qquad (A-4)$$

Equations (A-1) through (A-4) show that once $H - H^0$ and $A - A^0$ are evaluated, the other thermodynamic properties can be readily calculated.

Enthalpy Departure

In terms of reduced temperature T^*, and reduced density ρ^*, equation (A-1) becomes:

$$\frac{H - H^0}{RT} = -T \int_0^{\rho^*} \left(\frac{\partial Z}{\partial T^*}\right)_{\rho^*} \left(\frac{dT^*}{dT}\right) \frac{d\rho^*}{\rho^*} + (Z - 1) \qquad \text{(A-5)}$$

From equations (2), (13), (16) and (7)

$$T^* = kT/\epsilon_x$$

$$\sigma_x^{4.5}\epsilon_x = \Sigma\Sigma x_i x_j \sigma_{ij}^{4.5}\epsilon_{ij}$$

$$\epsilon_{ij} = \zeta_{ij}(\epsilon_i\epsilon_j)^{1/2}$$

$$\epsilon_i = \epsilon_{oi} + k\kappa_i/T$$

Differentiating T^* and ϵ,

$$\frac{dT^*}{dT} = \frac{k}{\epsilon_x}\left(1 - \frac{T}{\epsilon_x}\frac{d\epsilon_x}{dT}\right) \qquad \text{(A-6)}$$

$$\frac{d\epsilon_x}{dT} = -\frac{k}{2\sigma_x^{4.5}T^2} \Sigma\Sigma\, x_i x_j \sigma_{ij}^{4.5}\zeta_{ij}(\epsilon_i\epsilon_j)^{-1/2}(\epsilon_i\kappa_j + \epsilon_j\kappa_i) \qquad \text{(A-7)}$$

$$\frac{dT^*}{dT} = \frac{k}{\epsilon_x}\left(1 + \frac{T^*}{2\sigma_x^{4.5}T^2} \Sigma\Sigma\, x_i x_j \sigma_{ij}^{4.5}\zeta_{ij}(\epsilon_i\epsilon_j)^{-1/2}(\epsilon_i\kappa_j + \epsilon_j\kappa_i)\right) \qquad \text{(A-8)}$$

Differentiating Z from equation (1), with respect to $\tilde{T}$, then integrating, equation (A-5) becomes:

$$\frac{H - H^0}{RT} = \left[-T\frac{dT^*}{dT}\right]\left[\rho^*(E_2T^{*-2} + 3E_3T^{*-4} - 4E_9T^{*-5} + 5E_{11}T^{*-6}) + 0.5\rho^{*2}(E_6T^{*-2} + 2E_{10}T^{*-3}) + 0.2\rho^{*5}(-E_7T^{*-2} - 2E_{12}T^{*-3}) + \frac{3E_8T^{*-4}}{E_4}(e^{-E_4\rho^{*2}}(1 + 0.5E_4\rho^{*2}) - 1)\right] + (Z - 1)$$

(A-9)

Substituting (A-8) into (A-9), the final expression for $H - H^0$ can be obtained.

Fugacity

In terms of reduced density, equation (A-2) becomes:

$$\frac{A - A^0}{RT} = \int_0^{\rho^*}(Z - 1)\frac{d\rho^*}{\rho^*} - \ln\frac{V}{V^0} \qquad (A-10)$$

Substitute Z, from equation (1), into equation (A-10), then integrate, equation (A-10) becomes:

$$\frac{A - A^0}{RT} = \rho^*(E_1 - E_2T^{*-1} - E_3T^{*-3} + E_9T^{*-4} - E_{11}T^{*-5}) + 0.5\rho^{*2}(E_5 - E_6T^{*-1} - E_{10}T^{*-2}) + 0.2\rho^{*5}(E_7T^{*-1} + E_{12}T^{*-2}) - E_8T^{*-3}e^{-E_4\rho^{*2}}(\frac{1}{E_4} + 0.5\rho^{*2}) + \frac{E_8T^{*-3}}{E_4} - \ln\frac{V}{V^0} \qquad (A-11)$$

From equations (12), (13) and (14)

$$\sigma_x^{4.5} = \sum\sum_{ij} x_i x_j \sigma_{ij}^{4.5}$$

$$\varepsilon_x \sigma_x^{4.5} = \sum\sum_{ij} x_i x_j \varepsilon_{ij} \sigma_{ij}^{4.5}$$

$$\gamma_x \sigma_x^{3.5} = \sum\sum_{ij} x_i x_j \gamma_{ij} \sigma_{ij}^{3.5}$$

And from equation (A-4), the fugacity of the ith component in a mixture can be obtained by differentiating equation (A-11), with respect to n_i:

$$\ln\left(\frac{f_i}{x_i f_i^0}\right) = \frac{H - H^0}{RT} - \frac{S - S^0}{RT} + \bar{R}_i(Z - 1) + \bar{V}_i\left[\frac{H - H^0}{RT} - (Z - 1)\right]/\left(1 - \frac{T}{\varepsilon}\frac{d\varepsilon}{dT}\right)$$
$$+ \rho^*[\bar{B}_{1,i} - \bar{B}_{2,i}T^{*-1} - \bar{B}_{3,i}T^{*-3} + \bar{B}_{9,i}T^{*-4} - \bar{B}_{11,i}T^{*-5}]$$
$$+ \frac{\rho^{*2}}{2}[\bar{B}_{5,i} - \bar{B}_{6,i}T^{*-1} - \bar{B}_{10,i}T^{*-2}] + \frac{\rho^{*5}}{5}(\bar{B}_{7,i}T^{*-1} + \bar{B}_{12,i}T^{*-2})$$
$$+ \bar{B}_{8,i}T^{*-3}[1 - e^{-B_4\rho^{*2}} - \frac{1}{2}B_4\rho^{*2}e^{-B_4\rho^{*2}}]/B_4$$

(A-12)

where f_i^0 is the standard-state reference fugacity, taken to be unity. The derivatives in equations (A-12) are:

$$\bar{B}_{j,i} \equiv \left.\frac{\partial B_j}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= b_j \left.\frac{\partial \gamma_x}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= b_j \gamma_x \left[2\left(\frac{\sum_m x_m \gamma_{m_i} \sigma_{m_i}^{3.5}}{\gamma_x \sigma_x^{3.5}} - 1\right) - \frac{3.5}{3}\bar{R}_i\right] \qquad \text{(A-13)}$$

$$\bar{R}_i \equiv \frac{1}{\sigma^3} \left.\frac{\partial \sigma^3}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= \frac{6}{4.5}\left[\frac{\sum_m x_m \sigma_{m_i}^{4.5}}{\sigma_x^{4.5}} - 1\right] \qquad \text{(A-14)}$$

$$\bar{V}_i \equiv -\frac{1}{T^*} \left.\frac{\partial T^*}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= 2\left[\frac{\sum_m x_m \varepsilon_{m_i} \sigma_{m_i}^{4.5}}{\varepsilon_x \sigma_x^{4.5}} - 1\right] - \frac{4.5}{3}\bar{R}_i \qquad \text{(A-15)}$$

APPENDIX B

EXPRESSIONS FOR DERIVED THERMODYNAMIC PROPERTIES USING THE H.M.R.

Using the NMR, Equations (A-1) through (A-6) and (A-9) through (A-12) are still applicable. From equation (52)

$$\varepsilon_x = \Sigma\, x_i \frac{\Sigma\, x_j\, \varepsilon_{ij} \exp(-\Delta_{ij}/RT)}{\Sigma\, x_k \exp(-\Delta_{ik}/RT)}$$

Equation (A-7) becomes:

$$\frac{d\varepsilon_x}{dT} = -\frac{k}{2T^2}\,\Sigma\, x_i \frac{\Sigma x_j \zeta_{ij} (\varepsilon_i \varepsilon_j)^{-1/2} (\varepsilon_i \kappa_j + \varepsilon_j \kappa_i) e^{-\Delta_{ij}/RT}}{\Sigma x_k e^{-\Delta_{ik}/RT}}$$

$$+ \frac{1}{T^2}\,\Sigma\, x_i \frac{\Sigma x_j \varepsilon_{ij} (\Delta_{ij}/R) e^{-\Delta_{ij}/RT}}{\Sigma x_k e^{-\Delta_{ik}/RT}}$$

$$- \frac{1}{T^2}\,\Sigma\, x_i \frac{(\Sigma x_j \varepsilon_{ij} e^{-\Delta_{ij}/RT})\,(\Sigma x_k (\Delta_{ik}/R) e^{-\Delta_{ik}/RT})}{(\Sigma x_k\, e^{-\Delta_{ik}/RT})^2} \qquad \text{(B-1)}$$

From equations (52), (53) and (54)

$$\varepsilon_x = \Sigma\, x_i \frac{\Sigma\, x_j\, \varepsilon_{ij} \exp(-\Delta_{ij}/RT)}{\Sigma\, x_k \exp(-\Delta_{ik}/RT)}$$

$$\sigma_x^3 = \Sigma \Sigma\, x_i\, x_j\, \sigma_{ij}^3$$

$$\gamma_x\, \sigma_x^3 = \Sigma \Sigma\, x_i\, x_j\, \gamma_{ij}\, \sigma_{ij}^3$$

The derivatives in equation (A-12) become

$$\bar{B}_{j,i} \equiv \left.\frac{\partial B_j}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= b_j \left.\frac{\partial \gamma_x}{\partial n_i}\right|_{T,V,n_{k\neq i}} \qquad \text{(B-2)}$$

$$= b_j\, \gamma_x \left[2\left(\frac{\Sigma_m\, x_m \gamma_{m_i} \sigma_{m_i}^3}{\gamma_x\, \sigma_x^3} - 1\right) - \bar{R}_i \right]$$

$$\bar{R}_i \equiv \frac{1}{\sigma^3} \left.\frac{\partial \sigma^3}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= 2 \left[\frac{\Sigma_m\, x_m \sigma_{m_i}^3}{\sigma_x^3} - 1 \right] \qquad \text{(B-3)}$$

$$\bar{V}_i \equiv -\frac{1}{T^*} \left.\frac{\partial T^*}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= \frac{1}{\varepsilon_x} \left[\frac{\Sigma x_j \varepsilon_{ij} e^{-\Delta_{ij}/RT}}{\Sigma x_k e^{-\Delta_{ik}/RT}} + \Sigma\, x_m \frac{\varepsilon_{m_i} e^{-\Delta_{m_i}/RT}}{\Sigma x_k e^{-\Delta_{mk}/RT}} \right.$$

$$\left. + \Sigma\, x_m \frac{(\Sigma x_j \varepsilon_{mj} e^{-\Delta_{mj}/RT})\,(e^{-\Delta_{m_i}/RT})}{(\Sigma x_k e^{-\Delta_{mk}/RT})^2} - \varepsilon_x \right] \qquad \text{(B-4)}$$

APPENDIX C

Table C.1

Detailed Calculations of Vapor-Liquid Equilibria from the H.M.R. (see table VI.4 and Figure 3)

Ethane(1)-Acetone(2) Mixture
Data from Ohgaki et al., 1976

N	T(R)	P(PSIA)	X1(EXP)	X1(CAL)	DEV %	Y1(EXP)	Y1(CAL)	DEV %
1	536.67	69.674	0.0427	0.0416	-2.421	0.9371	0.9359	-0.122
2	536.67	142.683	0.0916	0.0910	-0.588	0.9647	0.9662	0.153
3	536.67	256.665	0.1720	0.1774	3.099	0.9769	0.9787	0.184
4	536.67	382.741	0.2826	0.2977	5.371	0.9809	0.9831	0.229
5	536.67	487.597	0.4485	0.4603	2.651	0.9819	0.9842	0.243
6	536.67	516.651	0.5770	0.5604	-2.864	0.9816	0.9843	0.268
7	536.67	525.645	0.6919	0.6571	-5.024	0.9821	0.9843	0.229
8	536.67	570.938	0.9268	0.9642	4.039	0.9841	0.9906	0.666

N	T(R)	P(PSIA)	X2(EXP)	X2(CAL)	DEV %	Y2(EXP)	Y2(CAL)	DEV %
1	536.67	69.674	0.9573	0.9583	0.108	0.0629	0.0640	1.831
2	536.67	142.683	0.9084	0.9089	0.059	0.0352	0.0337	-4.236
3	536.67	256.665	0.8279	0.8221	-0.644	0.0231	0.0212	-7.811
4	536.67	382.741	0.7174	0.7022	-2.115	0.0191	0.0168	-11.768
5	536.67	487.597	0.5515	0.5396	-2.156	0.0181	0.0157	-13.211
6	536.67	516.651	0.4230	0.4395	3.906	0.0183	0.0156	-14.376
7	536.67	525.645	0.3081	0.3429	11.290	0.0179	0.0157	-12.290
8	536.67	570.938	0.0732	0.0357	-51.143	0.0159	0.0093	-41.250

Table C.1 (Continued)

N	T(R)	P(PSIA)	K1(EXP)	K1(CAL)	DEV %	K2(EXP)	K2(CAL)	DEV %
1	536.67	69.674	21.946	22.463	2.35	0.06571	0.06684	1.72
2	536.67	142.683	10.532	10.611	0.74	0.03875	0.03709	-4.23
3	536.67	256.665	5.676	5.515	-2.82	0.02790	0.02589	-7.21
4	536.67	382.741	3.470	3.301	-4.88	0.02662	0.02400	-9.86
5	536.67	487.597	2.189	2.137	-2.34	0.03282	0.02911	-11.29
6	536.67	516.651	1.701	1.756	3.22	0.04326	0.03565	-17.59
7	536.67	525.645	1.419	1.497	5.53	0.05810	0.04564	-21.44
8	536.67	570.938	1.061	1.027	-3.24	0.21721	0.26120	20.25

NPTS = 8

% AARD OF K_1
3.14

% AARD OF K_2
11.70

% AARD OF X_1
3.25

% AARD OF X_2
8.92

% AARD OF Y_1
0.26

% AARD OF Y_2
13.38

Table C.2

Detailed Calculations of Vapor-Liquid Equilibria
from the CSM
(see table VI.4 and Figure 3)

Ethane(1)-Acetone(2) Mixture
Data from Ohgaki et al., 1976

N	T(R)	P(PSIA)	X1(EXP)	X1(CAL)	DEV %	Y1(EXP)	Y1(CAL)	DEV %
1	536.67	69.674	0.0427	0.0432	1.389	0.9371	0.9360	-0.115
2	536.67	142.683	0.0915	0.0922	0.691	0.9647	0.9661	0.143
3	536.67	256.665	0.1720	0.1734	0.765	0.9769	0.9783	0.153
4	536.67	382.741	0.2826	0.2817	-0.299	0.9809	0.9825	0.170
5	536.67	487.597	0.4485	0.4423	-1.363	0.9819	0.9833	0.146
6	536.67	516.651	0.5770	0.8696	50.719	0.9816	0.9845	0.292
7	536.67	525.645	0.6919	0.8940	29.216	0.9821	0.9854	0.345
8	536.67	570.938	0.9268	0.9683	4.485	0.9841	0.9924	0.848

N	T(R)	P(PSIA)	X2(EXP)	X2(CAL)	DEV %	Y2(EXP)	Y2(CAL)	DEV %
1	536.67	69.674	0.9573	0.9567	-0.062	0.0629	0.0639	1.723
2	536.67	142.683	0.9084	0.9077	-0.069	0.0352	0.0338	-3.926
3	536.67	256.665	0.8279	0.8265	-0.159	0.0231	0.0216	-6.486
4	536.67	382.741	0.7174	0.7182	0.117	0.0191	0.0174	-8.756
5	536.67	487.597	0.5515	0.5576	1.108	0.0181	0.0166	-7.963
6	536.67	516.651	0.4230	0.1303	-69.184	0.0183	0.0154	-15.679
7	536.67	525.645	0.3081	0.1059	-65.611	0.0179	0.0145	-18.954
8	536.67	570.938	0.0732	0.0316	-56.795	0.0159	0.0075	-52.507

Table C.2 (Continued)

N	T(R)	P(PSIA)	K1(EXP)	K1(CAL)	DEV %	K2(EXP)	K2(CAL)	DEV %
1	536.67	69.674	21.946	21.620	-1.48	0.06571	0.06688	1.78
2	536.67	142.683	10.532	10.475	-0.54	0.03875	0.03725	-3.85
3	536.67	256.665	5.675	5.641	-0.60	0.02790	0.02613	-6.33
4	536.67	382.741	3.470	3.487	0.47	0.02662	0.02426	-8.86
5	536.67	487.597	2.189	2.222	1.53	0.03282	0.02987	-8.97
6	536.67	516.651	1.701	1.132	-33.45	0.04326	0.11838	173.62
7	536.67	525.645	1.419	1.102	-22.34	0.05810	0.13692	135.67
8	536.67	570.938	1.061	1.024	-3.48	0.21721	0.23877	9.92

NPTS = 8

% AARD OF K_1
7.98

% AARD OF K_2
43.63

% AARD OF X_1
11.11

% AARD OF X_2
24.13

% AARD OF Y_1
0.27

% AARD OF Y_2
14.50

Table C.3

Detailed Calculations of Mixture Density
from the H.M.R.
(see table VI.4)

Methanol(1)-Benzene(2) Mixture
Data from Sumer and Thompson, 1967

N	T(R)	P(PSIA)	X1	DEN(EXP) LBMOLE/CU.FT.	DEN(CAL) LBMOLE/CU.FT.	% DEV
1	527.670	14.696	0.1104	1.3454	1.3557	0.76593
2	527.670	14.696	0.2208	1.2667	1.2623	-0.34265
3	527.670	14.696	0.3185	1.1946	1.1801	-1.21118
4	527.670	14.696	0.4251	1.1147	1.0919	-2.04594
5	527.670	14.696	0.5233	1.0402	1.0125	-2.66380
6	527.670	14.696	0.6324	0.9543	0.9271	-2.85713
7	527.670	14.696	0.7237	0.8807	0.8579	-2.59210
8	527.670	14.696	0.8171	0.8039	0.7895	-1.79023
9	527.670	14.696	0.9091	0.7264	0.7245	-0.27147
10	536.670	14.696	0.1673	1.3022	1.3158	1.04579
11	536.670	14.696	0.2670	1.2244	1.2312	0.55474
12	536.670	14.696	0.3783	1.1374	1.1377	0.02230
13	536.670	14.696	0.5060	1.0377	1.0331	-0.43757
14	536.670	14.696	0.6295	0.9412	0.9355	-0.60779
15	536.670	14.696	0.6313	0.9397	0.9341	-0.60481
16	536.670	14.696	0.7460	0.8503	0.8469	-0.39094
17	536.670	14.696	0.8765	0.7486	0.7522	0.48397
18	545.670	14.696	0.1103	1.3619	1.3727	0.79627
19	545.670	14.696	0.2206	1.2822	1.2786	-0.27907
20	545.670	14.696	0.3182	1.2097	1.1957	-1.16483
21	545.670	14.696	0.4248	1.1281	1.1065	-1.91536
22	545.670	14.696	0.5230	1.0519	1.0262	-2.44245
23	545.670	14.696	0.6322	0.9647	0.9396	-2.60537
24	545.670	14.696	0.7234	0.8908	0.8696	-2.38582
25	545.670	14.696	0.8169	0.8132	0.8002	-1.60496
26	545.670	14.696	0.9090	0.7349	0.7342	-0.09416
27	563.670	14.696	0.1103	1.3776	1.3900	0.90272
28	563.670	14.696	0.2205	1.2965	1.2952	-0.10107
29	563.670	14.696	0.3182	1.2237	1.2113	-1.01467
30	563.670	14.696	0.4248	1.1424	1.1211	-1.85650
31	563.670	14.696	0.5230	1.0655	1.0399	-2.39758
32	563.670	14.696	0.6321	0.9777	0.9523	-2.59249
33	563.670	14.696	0.7234	0.9015	0.8813	-2.23475
34	563.670	14.696	0.8169	0.8231	0.8110	-1.47713
35	563.670	14.696	0.9090	0.7437	0.7441	0.04749

% AARD	No. Points
1.27	35

Table C.4

Detailed Calculations of Mixture Density
from the CSM
(see table VI.4)

Methanol(1)-Benzene(2) Mixture
Data from Sumer and Thompson, 1967

N	T(R)	P(PSIA)	X1	DEN(EXP) LBMOLE/CU.FT.	DEN(CAL) LBMOLE/CU.FT.	% DEV
1	527.670	14.696	0.1104	1.3454	1.2780	-5.009
2	527.670	14.696	0.2208	1.2667	1.1219	-11.43
3	527.670	14.696	0.3185	1.1946	0.9967	-16.56
4	527.670	14.696	0.4251	1.1147	0.8765	-21.36
5	527.670	14.696	0.5233	1.0402	0.7837	-24.66
6	527.670	14.696	0.6324	0.9543	0.7042	-26.20
7	527.670	14.696	0.7237	0.8807	0.6598	-25.08
8	527.670	14.696	0.8171	0.8039	0.6371	-20.74
9	527.670	14.696	0.9091	0.7264	0.6384	-12.11
10	536.670	14.696	0.1673	1.3022	1.2031	-7.611
11	536.670	14.696	0.2670	1.2244	1.0676	-12.80
12	536.670	14.696	0.3783	1.1374	0.9328	-17.99
13	536.670	14.696	0.5060	1.0377	0.8037	-22.54
14	536.670	14.696	0.6295	0.9412	0.7106	-24.50
15	536.670	14.696	0.6313	0.9397	0.7095	-24.50
16	536.670	14.696	0.7460	0.8503	0.6565	-22.79
17	536.670	14.696	0.8765	0.7486	0.6395	-14.57
18	545.670	14.696	0.1103	1.3619	1.2939	-4.991
19	545.670	14.696	0.2206	1.2822	1.1361	-11.39
20	545.670	14.696	0.3182	1.2097	1.0096	-16.54
21	545.670	14.696	0.4248	1.1281	0.8879	-21.28
22	545.670	14.696	0.5230	1.0519	0.7940	-24.52
23	545.670	14.696	0.6322	0.9647	0.7135	-26.04
24	545.670	14.696	0.7234	0.8908	0.6685	-24.95
25	545.670	14.696	0.8169	0.8132	0.6456	-20.61
26	545.670	14.696	0.9090	0.7349	0.6469	-11.97
27	563.670	14.696	0.1103	1.3776	1.3100	-4.910
28	563.670	14.696	0.2205	1.2965	1.1504	-11.26
29	563.670	14.696	0.3182	1.2237	1.0223	-16.46
30	563.670	14.696	0.4248	1.1424	0.8992	-21.28
31	563.670	14.696	0.5230	1.0655	0.8042	-24.52
32	563.670	14.696	0.6321	0.9777	0.7229	-26.05
33	563.670	14.696	0.7234	0.9015	0.6774	-24.85
34	563.670	14.696	0.8169	0.8231	0.6542	-20.51
35	563.670	14.696	0.9090	0.7437	0.6556	-11.84

% AARD: 18.13

No. Points: 35

APPENDIX D

SOURCE LISTING OF HYBRID MIXING RULES SUBPROGRAM

```
      subroutine  es10  (t        ,p        ,x        ,ncp      ,idx
     $                  ,iwork    ,ijwork   ,kvl      ,kphi     ,kh
     $                  ,ks       ,kg       ,kv       ,nds      ,kdiag
     $                  ,phi      ,h        ,s        ,g        ,vio
     $                  ,dphi     ,dh       ,ds       ,dg       ,dvio
     $                  ,ker )
c-----------------------------------------------------------------------
c     Note*** ker=0   No error in root search
c               =1   Vapor root problem
c               =2   Liquid root problem
c
      implicit real*8 (a-h, o-z)
      common /espm/tstm,vstm,gstm
      common /hsrvb/hxx,sxx,ri,vi,bji
      common /pengy/pesp(4)
      common /dengy/pery(2)
      common /alpha/alfa1(4),alfa2(4),alfa3(4)
      common /ppglob/ pref,tref,rgas
      common /global/nh,in
      common /ncomp/ ncc
      common /codo/ mc
      common /tcbwr/ bwrtc(2)
      common /vcbwr/ bwrvc(2)
      common /bwrgma/ bwrgma(4)
      common /bwrkv/ bwrkv(4)
      common /bwrkt/ bwrkt(4)
      common /esbwrg/ bwrgij(4)
      common /bwrkvp/ bwrkvp(4)
      common /bwrktp/ bwrktp(4)
      common /bdkdt/ bdkdt(4)
      common /bdktii/ bdktii(4)
      common /dexdt/dexdt(4)
      common /ttt/temp
      common /bwrcon/ alph1,alph2,alph3,conv,cont
      common /eosbwr/ eos(10)
      common /esroot/ klflag, kvflag, pressl, pressv
      logical lv,ldv,lh,ldh,lg,ldg,lphi,ldphi,lsx,lhx,ldhx,ldvx
      logical ls, lds
      dimension   x(ncp), idx(ncp), phi(ncp), dphi(ncp)
      dimension ai(12), bi(12)
      dimension di(15),fij(4)
      data ai/1.45907d0,4.98813d0,2.20704d0,4.86121d0,4.59311d0,
     1 5.06707d0,11.4871d0,9.22469d0,.94624d-1,1.48858d0,.15273d-1,
```

```
     2 3.51486d0 /
      data bi /.32872d0,-2.64399d0,11.3293d0,0d0,2.79979d0,10.3901d0,
     1 10.3730d0,20.5388d0,2.7601d0,-3.11349d0,.18915d0,.94260d0 /
c
c        initial calculations
c
      temp=t
      ker=0
      rt=rgas*t
      pbrt=p/rt
c
c        set multiple data set index to be added to component index
c
      ids1=ncc*(nds-1)
      ids2=ncc*ids1
c
c        set logical variables which control calculation
c
      lv=kv.eq.1.or.kv.eq.3
      ldv=kv.gt.1
      lh=kh.eq.1.or.kh.eq.3
      ldh=kh.gt.1
      lg=kg.eq.1.or.kg.eq.3
      ldg=kg.gt.1
      ls=ks.eq.1 .or. ks.eq.3
      lds=ks.gt.1
      lphi=kphi.eq.1.or.kphi.eq.3
      ldphi=kphi.gt.1
      lsx=kg.ge.1.or.lphi.or.ls
      lhx=lh.or.lg.or.kphi.ge.1
      ldhx=ldh.or.ldphi.or.lds
      ldvx=ldv.or.ldhx
c
c        calculate mole fraction averaged quantities
c
      vstma=0d0
      tstm=0d0
      gstm=0d0
c
      do 200 i=1,ncp
      is=idx(i)
      xi=x(i)
      loci=ncc*(is-1)+ids2
      locii=loci+is
      xisq=xi*xi
      vstma=vstma+xisq*bwrkv(locii)
      gstm=gstm+xisq*bwrgij(locii)
      if (i.eq.ncp) go to 210
      j1=i+1
      xi2=2d0*xi
c
         do 200 j=j1,ncp
         js=idx(j)
```

```
            xij=xi2*x(j)
            locij=loci+js
            vstma=vstma+xij*bwrkv(locij)
            gstm=gstm+xij*bwrgij(locij)
c
  200   continue
c
  210   vstm=vstma**(1d0/alph1)
        vstm2=vstm**alph2
        vstm3=vstm**alph3
        gstm=gstm/vstm3
        fij(1)=1d0
        fij(2)=1d0
        fij(3)=1d0
        fij(4)=1d0
        tst=0d0
        do 55 i=1,ncp
        loij=ncc*(i-1)+i
        tes1=0d0
        tes2=0d0
        do 56 j=1,ncp
        loc=ncc*(i-1)+j
        tes=x(j)*fij(loc)*dexp(-pesp(loc)/t)
        tes1=tes1+tes*bwrkt(loc)
        tes2=tes2+tes
   56   continue
        tst=tst+x(i)*tes1/tes2
   55   continue
        tstm=tst
c
c          calculate reduced temp and powers
c
        tr1=tstm/t
        tr2=tr1*tr1
        tr3=tr2*tr1
        tr4=tr3*tr1
        tr5=tr4*tr1
c
c          calc bwr params
c
        b1=ai(1)+gstm*bi(1)
        b2=(ai(2)+gstm*bi(2))*tr1
        b3=(ai(3)+gstm*bi(3))*tr3
        b4=ai(4)
        b5=ai(5)+gstm*bi(5)
        b6=(ai(6)+gstm*bi(6))*tr1
        b7=(ai(7)+gstm*bi(7))*tr1
        b8=(ai(8)+gstm*bi(8))*tr3
        b9=(ai(9)+gstm*bi(9))*tr4
        b10=(ai(10)+gstm*bi(10))*tr2
        b11=(ai(11)+gstm*bi(11))*tr5
        b12=(ai(12)+gstm*bi(12))*tr2
c
```

```
c        calc coeffs of density in compr eqn
c
      trh1=b1-b2-b3+b9-b11
      trh2=b5-b6-b10
      trh5=b7+b12
c
c        solve for appropriate vol root using vproot or lqroot
c
      iflag=1
      k=4
      dpdv=-1000.d0
      vcm=vstm/(dsqrt(alfa1(1)*alfa1(2)))
      vlim=vcm/4d0
      vcmech=vcm
      vcut=vlim
      if (kvl.eq.2) vcut=1.2d0*vcm
c
         if (ncp .eq. 1 .and. kvl .eq. 1) kvflag=-1
         if (ncp .eq. 1 .and. kvl .eq. 2) klflag=-1
c
      go to (220, 230) , kvl
c
c     vapor properties calculation
c
 220  call vproot(k       ,iflag   ,vlim    ,vcmech ,vcut    ,
     1            t       ,p       ,v       ,pcalc  ,dpdv    ,
     2            iprog   ,kdiag   )
      go to (250,250,250,260,270), k
c
c     liquid properties calculation
c
 230  call lqroot(k       ,iflag   ,vlim    ,vcmech ,vcut    ,
     1            t       ,p       ,v       ,pcalc  ,dpdv    ,
     2            iprog   ,kdiag   )
      go to (250,250,250,260,270), k
c
c        pressure and dpdv calc
c
 250  rhr=vstm/v
      rhr2=rhr*rhr
      rhr3=rhr2*rhr
      rhr4=rhr3*rhr
      rhr5=rhr2*rhr2*rhr
      rhr6=rhr5*rhr
      rhr7=rhr6*rhr
      rhr8=rhr7*rhr
      b4rh=b4*rhr2
      b4rhe=dexp(-b4rh)
      rhr1t=rhr*trh1
      rhr2t=rhr2*trh2
      rhr5t=rhr5*trh5
      rhret=b8*rhr2*b4rhe
      z=1d0+rhr1t+rhr2t+rhr5t+rhret*(1d0+b4rh)
```

```
      rtbv=rt/v
      pcalc=z*rtbv
      if (iflag.ne.2) go to 878
      go to 871
 878  dpdv=-rtbv/v*(1d0+2d0*rhr1t+3d0*rhr2t+6d0*rhr5t+rhret*
     1        (3d0+b4rh*(3d0-2d0*b4rh)))
871   go to (220,230), kvl
c
c     convergence not achieved
c
 270  ker=kvl
      if (kdiag .lt. 2) go to 260
      err=pcalc/p-1d0
      write (nh,100) p,err
 100  format (6x,30hvolume convergence failed; p =  d11.4,18h fract err
     1 in p =  d12.4)
c
c        calculation of common terms
c
260   if(mc.eq.1.or.mc.eq.-1) go to 320
      dlz=dlog(z)
      ron=1d0/v
c     write(6,6666)z,ron
c6666  format(1x,'z,r',2g15.6)
      dlpr=dlog(pcalc/pref)
      pbrt=pcalc/rt
      b8b4e=b8/b4*b4rhe
      rbv=rgas/v
      b4rher=1d0/b4rhe
      dro=rhr1t+rhr2t/2d0+rhr5t/5d0+b8/b4*(1d0-b4rhe-0.5d0*b4rh*b4rhe)
      su0=0d0
      su1=0d0
      do 75 i=1,ncp
      lop=ncc*(i-1)+i
      se1=0d0
      se2=0d0
      se3=0d0
      se4=0d0
      do 76 j=1,ncp
      lok=ncc*(i-1)+j
      ses=x(j)*fij(lok)*dexp(-pesp(lok)/t)
      se1=se1+ses*(bdkdt(lok)-
     &  dexdt(lok)*bwrkt(lok))
      se2=se2+ses
      se3=se3+ses*bwrkt(lok)
      se4=se4+ses*dexdt(lok)
 76    continue
      su0=su0+x(i)*se1/se2
      su1=su1+x(i)*se3*se4/se2/se2
 75    continue
      sht=(su0+su1)/tstm+1d0
c
c        calculation of dv
```

```
c
      if (.not.ldvx) go to 300
      if (iflag.eq.2)
     1   dpdv=-rtbv/v*(1d0+2d0*rhr1t+3d0*rhr2t+6d0*rhr5t+rhret*
     2         (3d0+b4rh*(3d0-2d0*b4rh)))
      dpdt=rbv*(1d0+rhr*(b1+2d0*b3-3d0*b9+4d0*b11)
     1     +rhr2*(b5+b10)-rhr5*b12-2d0*rhret*(1d0+b4rh))
      dv=-dpdt/dpdv
c
c        calculation of enthalpy and its temp deriv
c
 300  if (lhx) go to 879
      go to 872
 879  hx=rt*((rhr*(b1-2d0*b2-4d0*b3+5d0*b9-6d0*b11)
     1             +rhr2*(b5-1.5d0*b6-2d0*b10)+rhr5*(1.2d0*b7+1.4d0*b12
     2             +b8b4e*(3d0/b4rhe-3d0-b4rh*(5d-1-b4rh)))
     3             *sht+(z-1d0)*(1d0-sht))
      hxx=hx
872   if(mc.ne.0)go to 320
      if (.not.ldhx) go to 310
      dhdt=rgas*(rhr*(b1+8d0*b3-15d0*b9+24d0*b11)
     1     +rhr2*(b5+2d0*b10)-1.4d0*rhr5*b12
     2     -2d0*b8b4e*(3d0/b4rhe-3d0-b4rh*(5d-1-b4rh)))
      dhdv=-rtbv*(rhr*(b1-2d0*b2-4d0*b3+5d0*b9-6d0*b11)
     1     +2d0*rhr2*(b5-1.5d0*b6-2d0*b10)+rhr5*(6d0*b7+7d0*b12)
     2     +rhret*(5d0+b4rh*(5d0-2d0*b4rh)))
      dhx=dhdt+dv*dhdv
c
c        calculation of entropy
c
 310  if (lsx) go to 881
      go to 873
 881  sx=rgas*((-rhr*(b1+2d0*b3-3d0*b9+4d0*b11)
     1    -5d-1*rhr2*(b5+b10)+2d-1*rhr5*b12
     2    +2d0*b8b4e*(b4rher-1d0-5d-1*b4rh))*sht-dro*(1d0-sht)
     3    +dlz-dlpr)
      sxx=sx
c
c-----------------------------------------------------------------------
c
c        calculation of fugacity coeffs and temp derivs
c
c-----------------------------------------------------------------------
c
 873  if (kphi.le.0) go to 320
c
c        begin calc of comp dep bwr consts
c
      b1=bi(1)
      b2=bi(2)*tr1
      b3=bi(3)*tr3
      b5=bi(5)
      b6=bi(6)*tr1
```

```
      b7=bi(7)*tr1
      b8=bi(8)*tr3
      b9=bi(9)*tr4
      b10=bi(10)*tr2
      b11=bi(11)*tr5
      b12=bi(12)*tr2
      b8b4e=b8/b4*b4rhe
c
c        calculation of common terms
c
      zmo=z-1d0
      hxrt=hx/rt
      trh1=rhr*(b1-b2-b3+b9-b11)
      trh2=rhr2*(b5-b6-b10)
      trh5=rhr5*(b7+b12)
c
c        calc coeffs of comp derivs of vst,tst,gma for fug
c
      if (.not.lphi) go to 410
      coeff0=hxrt-sx/rgas-dlpr
      if (kvl .eq. 2) coeff0=coeff0-dlog(p/pcalc)
      coeffv=hxrt-zmo
      coeffr=zmo
      coeffb=trh1*5d-1*trh2*2d-1*trh5+b8b4e*(b4rher-1d0-5d-1*b4rh)
c
c        calc coeffs of comp derivs of vst,tst,gst for fug deriv
c
 410  if (.not.ldphi) go to 420
      hxrtt=hxrt/t
      coefd0=-hxrtt
      fn=z/t-pbrt*dv
      coefdv=-hxrtt+dhx/rt+fn
      coefdr=-fn
      fnt=rhr*((b2+3d0*b3-4d0*b9+5d0*b11)
     1    +5d-1*rhr2*(b6+2d0*b10)-2d-1*rhr5*(b7+2d0*b12)
     2    -b8b4e*(b4rher-1d0-5d-1*b4rh))
      fnv=trh1+trh2+trh5-b8b4e*(1d0+b4rh)
      coefdb=fnt/t-fnv*dv/v
c
c        calculation of fug coeffs and temp derivs
c
420   rt1=2d0/alph1
      bjt1=2d0/vstm3
c
      do 430 i=1,ncp
      lopi=ncc*(i-1)+i
      is=idx(i)
      loci=ncc*(is-1)+ids2
c
         vsti=0d0
         gsti=0d0
         tsti1=0d0
         tsti2=0d0
```

```
          tsti3=0d0
          tsti4=0d0
          do 440 j=1,ncp
          lopj=ncc*(j-1)+j
          js=idx(j)
          locij=loci+js
          xj=x(j)
          vsti=vsti+xj*bwrkv(locij)
          gsti=gsti+xj*bwrgij(locij)
          tss1=0d0
          tss2=0d0
          do 441 k3=1,ncp
          ko=ncc*(j-1)+k3
          ses1=x(k3)*fij(ko)*dexp(-pesp(ko)/t)
          tss1=tss1+ses1*bwrkt(ko)
          tss2=tss2+ses1
441       continue
          kw=locij
          if(locij.eq.2) kw=3
          if(locij.eq.3) kw=2
          tsti1=tsti1+xj*fij(locij)*bwrkt(locij)
     1     *dexp(-pesp(locij)/t)
          tsti2=tsti2+xj*fij(locij)*dexp(-pesp(locij)/t)
          tsti3=tsti3+xj*fij(kw)*bwrkt(kw)
     1     *dexp(-pesp(kw)/t)/tss2
          tsti4=tsti4+xj*fij(kw)*dexp(-pesp(kw)/t)*tss1/tss2/tss2
 440      continue
c
      ri=rt1*(vsti/vstma-1d0)
      vi=(-tstm+tsti1/tsti2+tsti3-tsti4)/tstm
      vi=vi/sht
      bji=bjt1*gsti-(2d0+alph3*ri)*gstm
c       calc of fug. coef. of zalpha
c
      if (lphi) go to 3333
      go to 3322
3333  phi(i)=coeff0+ri*coeffr+vi*coeffv+bji*coeffb
c     write(6,4444) i,phi(i),x(i)
c4444  format(1x,'i,fi',i5,2g15.6)
3322  if (ldphi) dphi(i)=coefd0+ri*coefdr+vi*coefdv+bji*coefdb
 430  continue
      vio=v
c
c        return output quantities as requested
c
 320  h=hx
      if (lv) vio=v
      if (ldv) dvio=dv
c     if (lh) h=hx
      if (ldh) dh=dhx
      if (lg) g=hx-t*sx
      if (ldg) dg=-sx
      if (ls) s=sx
```

```
      if (lds) ds=dhx/t
      h=hx
      s=sx
c
      return
      end


      subroutine es11
c-----------------------------------------------------------
c     module title - initialization of CSM-3PCS-MBWR
c-----------------------------------------------------------
      implicit real*8 (a-h,o-z)
      common /ppglob/ pref,tref,rgas
      common /ttt/t
      common /alpha/alfa1(4),alfa2(4),alfa3(4)
      common /ncomp/ ncc
      common /tcbwr/ bwrtc(2)
      common /vcbwr/ bwrvc(2)
      common /bwrgma/ bwrgma(4)
      common /bwrkv/ bwrkv(4)
      common /bwrkt/ bwrkt(4)
      common /bdkdt/ bdkdt(4)
      common /esbwrg/ bwrgij(4)
      common /bwrkvp/ bwrkvp(4)
      common /bwrktp/ bwrktp(4)
      common /bdktii/ bdktii(4)
      common /pengy/pesp(4)
      common /dengy/ pery(2)
      common /dexdt/dexdt(4)
      common /bwrcon/ alph1,alph2,alph3,conv,cont
      data alph1d,alph2d,alph3d/3.0d0,3.0d0,3.0d0/
c        set constants from data
      alph1=alph1d/3.d0
      alph2=alph2d/3.d0
      alph3=alph3d/3.d0
      do 120 i=1,ncc
      in=i
      dmi=alfa3(in)/t
      tci=bwrtc(in)/alfa2(in)+dmi
      vci=bwrvc(in)*alfa1(in)
      gmai=bwrgma(in)
      loci=ncc*(i-1)
      locii=loci+i
      bwrkvp(locii)=1d0
      bwrktp(locii)=1d0
c
         do 120 j=i,ncc
         jn=j
         dmj=alfa3(jn)/t
         tcj=bwrtc(jn)/alfa2(jn)+dmj
         vcj=bwrvc(jn)*alfa1(jn)
```

```
            gmaj=bwrgma(jn)
            ji=ncc*(i-1)+j
            vji=bwrkvp(ji)
            vstij=vji*vji*vji*dsqrt(vci*vcj)
            bwrkv(ji)=vstij**alph1
            bdkdt(ji)=0.5d0*bwrktp(ji)*(tcj*dmi+tci*dmj)/dsqrt(tci*tcj)
            bwrkt(ji)=bwrktp(ji)*dsqrt(tci*tcj)
            bwrgij(ji)=5d-1*(gmai+gmaj)*vstij**alph3
         ij=ncc*(j-1)+i
         bwrkv(ij)=bwrkv(ji)
         bdkdt(ij)=bdkdt(ji)
         bwrkt(ij)=bwrkt(ji)
         bwrgij(ij)=bwrgij(ji)
120      continue
         pesp(1)=0d0
         pesp(4)=0d0
         pesp(2)=pery(1)
         pesp(3)=pery(2)
         dexdt(2)=pery(1)/t
         dexdt(3)=pery(2)/t
         dexdt(1)=0d0
         dexdt(4)=0d0
         continue
         return
         end
```