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AJLAN, MOHAMMAD-HASSAN ABDUL-RAZZAG

USE OF CONFORMAL SOLUTION MODELS FOR PREDICTION OF POLAR, POLYATOMIC FLUID MIXTURE TRANSPORT PROPERTIES

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GRADUATE COLLEGE

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A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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degree of

DOCTOR OF PHILOSOPHY

BY

MOHAMMAD-HASSAN ABDUL-RAZZAG AJLAN

Norman, Oklahoma

1981

USE OF CONFORMAL SOLUTION MODELS FOR PREDICTION OF POLAR, POLYATOMIC FLUID MIXTURE TRANSPORT PROPERTIES

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ABSTRACT

Conformal solution theory models for the prediction of mixture viscosity and thermal conductivity are investigated. The models predicted these properties with reasonable accuracies for wide ranges of systems and conditions.

The modified Van der Waals one fluid model, set A, predicted binary mixture properties with average absolute deviations from experimental data of (1) 3.73% for dilute gas viscosity (1.63% for nonpolar-nonpolar, 3.28% for polar-polar, 4.75% for nonpolar-polar and 3.29% for associating-associating binary pairs), (2) 10.45% for dense fluid and liquid viscosity (9.19% for nonpolar-nonpolar, 21.21% for nonpolar-polar, 13.53% for associating-associating, 17.21% for nonpolar-associating and 7.24% for polar-associating binary pairs), (3) 3.37% for dilute gas thermal conductivity (2.68% for nonpolar-nonpolar, 3.10% for polar-polar and 4.64% for nonpolar-polar binary pairs) and (4) 11.41% for dense fluid and liquid thermal conductivity (4.73% for nonpolar-nonpolar, 8.11% for nonpolar-polar, 8.38% for polar-polar, 14.66% for associating-associating, 12.79% for nonpolar-associating and 13.47% for polar-associating binary pairs).

The so-called semiempirical model, set B, predicted binary mixture properties with accuracies comparable to the modified van der Waals one fluid model. The average absolute deviations of predicted binary mixture properties from experimental data by set B were (1) 3.51% for dilute gas viscosity (2.43% for nonpolar-nonpolar, 3.34% for polar-polar, 4.02% for nonpolar-polar and 3.45% for associating-assciating binary pairs), (2) 10.37% for dense fluid and liquid viscosity (8.92% for nonpolar-nonpolar, 21.75% for nonpolar-polar, 13.77% for associating-associating, 17.12% for nonpolar-associating and 9.27% for polar-associating binary pairs), (3) 3.05% for dilute gas thermal conductivity (2.50% for nonpolar-nonpolar, 3.96% for nonpolar-polar and 3.10% for polar-polar binary pairs) and (4) 11.44% for dense fluid and liquid thermal conductivity (4.60% for nonpolar-nonpolar, 7.52% for nonpolar-polar, 8.00% for polar-polar, 15.15% for associating-associating, 12.43% for nonpolar-associating and 12.01% for polar-associating binary pairs).

Also, an empirical model for the viscosity prediction of nonpolar mixtures is presented. This empirical model, which is not a conformal solution model, predicts the viscosity of nonpolar mixtures with average absolute deviations of 1.73% for dilute gas binary mixtures and 7.22% for dense fluid and liquid binary mixtures.

Models developed in this work can be used for practical industrial calculations of mixture viscosity and thermal

conductivity. Probably no other correlation covers such a wide range of systems and conditions with a single formulation.

CHAPTER I

INTRODUCTION

Prediction of the transport properties of mixtures are important for engineering design. The prediction of viscosity and thermal conductivity of mixtures is addressed in this work.

The models presented here are based on conformal solution theory, in which the main assumption is that all conponents of the mixtures (a,b,c...n) are conformal, that is, they obey the same intermolecular pair potential law. The model used here assumes a hypothetical pure fluid with characteristic parameters obtained from mixing rules involving the pure component parameters, composition and perhaps binary unlike interaction parameters, so that the mixture properties can be approximated by those of the hypothetical pure fluid.

The application of this method has been successful in predicting the thermodynamic properties of nonpolar mixtures (69,70,74,86,96,108,112,113). The extension of the method to transport properties prediction has been proposed by many investigators. Mo and Gubbins (84) presented conformal solution models for the prediction of the viscosity and thermal conductivity of isotropic mixtures and these models

were extended by Starling, et al (69) to cover hydrocarbon mixtures in the C_1-C_{10} carbon range. Recently, Ely and Hanley (28) have presented a model for viscosity prediction which covers a wide range of hydrocarbon mixturs.

All of the above models are restricted to certain mixture types and no models have been successful for mixtures of higher hydrocarbons, polar or associated components. The objective of this study was then to cover wider classes of mixtures. The multiparameter corresponding state viscosity and thermal conductivity correlations for pure fluids presented by Chung (19) were applied in this study along with the conformal solution model mixing rules and the necessary combining rules to predict mixture transport properties. The mixing rules are required to evaluate the characteristic parameters for the hypothetical fluid, the separation parameters, σ_x, the energy parameter, ε_x, the acentric factor, ω_x, the dipole moment, μ_x, and the reduced mass, m^*_x, which are required by the multiparameter corresponding state correlations.

An empirical model is also presented for viscosity prediction of nonpolar mixtures at all possible temperature and pressure conditions. This model is based on expressing the coefficients of the viscosity correlation as functions of the coefficients of each compound in the mixture and the mixture composition. This model was found to predict the

viscosities of mixtures similar to natural gas with the highest accuracy.

Mixtures treated in this work cover such fluids as monatomic, nonpolar, polar and associated polyatomics at temperature and pressure conditions from the dilute gas phase to the liquid phase. A study of this scope has never been done before, and though this work by no means is complete, it certainly provides much needed information.

CHAPTER II

LITERATURE SURVEY

This chapter is intended to provide a brief summary on the state of the availability of correlations for the prediction of transport properties of mixtures.

Most of the available correlations are limited to narrow ranges of applications such as the dilute gaseous state, dense gaseous state or liquid state. Also, the correlations are limited in most of the cases to one kind of mixture such as nonpolar, polar-nonpolar or polar mixtures with association forces. Some of the liquid mixture methods also depend on the availability of the pure component properties at the same conditions as the mixture. A good summary of many of the available methods and their ranges of application is given in reference (98).

2.1 VISCOSITY

2.1.1 Dilute Gas Mixtures

The most used viscosity equation for dilute gases is derived from the Chapman-Enskog theory (49), which assumes:

1. Very dilute gas, so only binary collisions occur.
2. Molecular motion can be described by classical mechanics.
3. Intermolecular potential is spherically symmetrical.
4. Elastic collision occurs only.

The above assumptions narrow the range of application of this theory to monatomic gases at low pressures and high temperatures. But a variety of expressions were determined to extend its application to polyatomic fluids. The final Chapman-Enskog relation for pure fluids is:

$$\eta = \frac{(5/16)(\pi MRT)^{\frac{1}{2}}}{\pi\sigma^2\Omega_v} \tag{2.1.1}$$

$$= 26.693 \frac{\sqrt{MT}}{\sigma^2\Omega_v} \tag{2.1.2}$$

where Ω_v is the collision integral which would reduce to unity if there were no attraction forces between molecules. The collision integral is usually determined as a function of the reduced temperature, $T^* = \frac{kT}{\varepsilon}$ where k is Boltzmann's constant, T is the absolute temperature and ε is a characteristic

energy. Values of the collision integral are available for various potential functions, including the Lennard-Jones (12-6) potential,

$$\phi(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] \qquad (2.1.3)$$

where r is the distance between the molecule pair, σ is the characteristic distance defined as the distance r at zero potential and ε is the characteristic energy defined as the depth of the potential well at the potential minimum.

Although the Chapman-Enskog theory can be extended to mixtures, most mixture viscosity correlations have had some elements of empiricism introduced. The expression for mixtures viscosity can be written in the form

$$\eta_m = \sum_{i=1}^{n} \frac{x_i \eta_i}{x_i + \sum_{\substack{j=1 \\ j\neq i}}^{n} x_j \phi_{ij}} \qquad (2.1.4)$$

where η_m is the mixture viscosity, η_i is the pure gas viscosity for the ith compoent, x_i is the mole fraction of the ith component, n is the number of mixture components, and ϕ_{ij} is an interaction parameter which is related ot the binary diffusion coefficient D_{ij} and the densities of the pure components of the mixtures. Equation (2.1.4) was originally written in the more general form as

$$\eta_m = \sum_{i=1}^{n} \frac{x_i \eta_i}{x_i + \sum_{\substack{j=1 \\ j\neq i}}^{n} x_j \frac{(1.385\eta_i)}{\rho_i D_{ij}}} \qquad (2.1.5)$$

Thus, ϕ_{ij} is represented by

$$\phi_{ij} = 1.385 \frac{\eta_i}{\rho_i D_{ij}} \tag{2.1.6}$$

Most of the uncertainty in estimating the mixture viscosity lies in the values of D_{ij}, which are obtained from empirical formulas most of the time. Therefore, the parameter ϕ_{ij} was introduced to eliminate the use of D_{ij}, as will be shown subsequently.

The parameter ϕ_{ij} has been the subject of many investigations and many methods are available in the literature to estimate it. The most widely used methods are briefly mentioned below.

a. Wilke's Equation:

Wilke (130) introduced his expression for ϕ_{ij} to estimate that parameter for dilute nonpolar gas mixtures. This expression was found to work well for many mixtures (98). Wilke's expression for ϕ_{ij} is

$$\phi_{ij} = \frac{[1 + (\eta_i/\eta_j)^{1/2} (M_j/M_i)^{1/4}]^2}{(4/\sqrt{2}) [1 + (M_i/M_j)]^{1/2}} \tag{2.1.7}$$

and

$$\phi_{ji} = (\eta_j/\eta_i)(M_i M_j)\phi_{ij} \tag{2.1.8}$$

where M_i is the molecular weight of component i in the mixture.

b. Brokaw's Equation:

This is a method for the estimation of ϕ_{ij} which can be applied to polar-polar and polar-nonpolar mixtures as well as nonpolar-nonpolar (12). Brokaw's equation is

$$\phi_{ij} = (\eta_i/\eta_j)^{\frac{1}{2}} S_{ij} A_{ij} \tag{2.1.9}$$

where S_{ij} and A_{ij} are quantities defined below. S_{ij} is given by Brokaw as the following relation

$$S_{ij} = S_{ji} \approx \frac{1 + (T_i^* T_j^*)^{\frac{1}{2}} + (\delta_i \delta_j/4)}{[1 + T_i^* + \delta_i^2/4]^{\frac{1}{2}}[1+T_j^* + \delta_j^2/4]^{\frac{1}{2}}} \tag{2.1.10}$$

In principle S_{ij} and S_{ji} should reduce to unity if mixtures are nonpolar. However, equation (2.1.10) for S_{ij} is just an approximation, S_{ij} does not reduce to unity for nonpolar mixtures and precaution therefore must be taken in this case. The term δ is a dimensionless polar term which is defined as

$$\delta = \tfrac{1}{2} \frac{\mu^2}{\varepsilon \sigma^3} \tag{2.1.11}$$

where μ is the dipole moment in debye and σ and ε are the characteristic parameters obtained in this case from the Stockmayer potential,

$$\phi(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6} - g\delta(\frac{\sigma}{r})^{3}] \tag{2.1.12}$$

where

$$g = \tfrac{1}{2}[2 \operatorname{Cos} \theta_a \operatorname{Cos} \theta_b - \operatorname{Sin} \theta_a \operatorname{Sin} \theta_b \operatorname{Cos} \psi] \tag{2.1.13}$$

in which θ_a and θ_b are the angles of inclination of the dipole axes to the line joining the centers of the molecules and ψ is the azimuthal angle between them. Note that equation (2.1.12) reduces to the Lennard-Jones equation (2.1.3) in the limit when the dipole moment is zero. Brokaw recommends that if either δ_i or δ_j is greater than 0.1, then equation (2.1.10) must be used. The term A_{ij} in equation (2.1.9) is defined as

$$A_{ij} = C_{ij}(M_j/M_i)^{1/2}\left[1 + \frac{(M_iM_j) - (M_i/M_j)^{0.5}}{2(1+M_i/M_j) + \frac{1+(M_i/M_j)^{0.45}}{(1+C_{ij})}C_{ij}}\right] \quad (2.1.14)$$

where

$$C_{ij} = [4M_iM_j/(M_i + M_j)^2]^{1/2} \quad (2.1.15)$$

Both Wilke's equation (2.1.7) and Brokaw's equation (2.1.9) can be applied to nonpolar mixtures with almost comparable results, but for polar-nonpolar and polar-polar mixtures, Brokaw's method must be used.

Other methods appear in the literature in which the parameter ϕ_{ij} in equation (2.1.4) is not considered. The method proposed by Mason and Monchick (87) for the viscosity prediction of polar gas mixtures is worth mentioning because it takes into consideration the dipole moment effect on viscosity. The method is based on the Chapman-Enskog theory, was originally proposed for pure polar gases only, and was

later extended to polar mixtures (88). The model for pure components is,

$$\eta = (5/16)\left(\frac{mkT}{\pi}\right)^{\frac{1}{2}} \frac{f\eta}{\sigma^2 \Omega^{(2,2)*}} \tag{2.1.16}$$

and

$$f\eta = 1 + \frac{3}{198}\left[8\left(\frac{\Omega^{(2,3)*}}{\Omega^{(2,2)*}}\right) - 7\right] \tag{2.1.17}$$

where $f\eta$ is a correction factor which results from higher kinetic-theory approximations. $f\eta$ is usually around unity. The collision integrals $\Omega^{(2,2)*}$ and $\Omega^{(2,3)*}$ are based on the Stockmayer potential, equation (2.1.12) and are tabulated by Monchick and Mason (87) as functions of the reduced temperature, T^*, and δ, the polar term defined in equation (2.1.11).

Equations (2.1.16) and (2.1.17) also have been extended (88) to predict the viscosity of dilute polar gas mixtures by using the following combining rules,

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{\frac{1}{2}} \tag{2.1.18}$$

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \tag{2.1.19}$$

$$\delta_{ij} = (\delta_i \delta_j)^{\frac{1}{2}} \left[\frac{\sigma_i \sigma_j)^{\frac{1}{2}}}{\sigma_{ij}}\right]^3 \tag{2.1.20}$$

The binary mixture viscosity is calculated by the relation

$$\eta_m = \left[\frac{x_1^2}{H_{11}} + \frac{x_2^2}{H_{22}} - \frac{2x_1x_2H_{12}}{H_{11}H_{22}}\right]\left[1 - \frac{H_{12}^2}{H_{11}H_{22}}\right]^{-1} \tag{2.1.21}$$

where,

$$H_{11} = \frac{x_1^2}{\eta_1} + \frac{2x_1x_2RT}{(M_1+M_2P(D_{12})} \left[1+ \frac{3M_2A_{12}^*}{5M_1}\right] \tag{2.1.22}$$

$$H_{12} = \frac{2x_1x_2RT}{M_1+M_2P(D_{12})} \left[1-\frac{3}{5} A_{12}^*\right] \tag{2.1.23}$$

$$D_{12} = \frac{2.628 \times 10^{-3} T^{\frac{3}{2}}}{P\sigma_{12}^2 \Omega_{12}^{(1,1*)}} \left[\frac{M_1+M_2}{2M_1M_2}\right]^{\frac{1}{2}} \tag{2.1.24}$$

and

$$A_{12}^* = \Omega_{12}^{(2,2)*}/\Omega_{12}^{(1,1)*} \tag{2.1.25}$$

where T is the absolute temperature, P is the pressure, and x_i is the mole fraction of the ith component of the mixture. The collision integrals $\Omega_{12}^{(1,1)*}$ and $\Omega_{12}^{(2,2)*}$ are tabulated as connections of $T^* = \kappa T/\varepsilon_{12}$ and the polar term δ_{12} by Mason and Monchick in reference (87). The diffusion coefficient D_{21} is calculated by interchanging the subscripts of equation (2.1.24) and A_{21} is obtained in the same manner using equation (2.1.25).

The authors (88) tested the above approach with several polar-polar and polar-nonpolar mixtures and the results obtained were satisfactory in most of the cases.

Lee, Starling, Dolan and Ellington (66) proposed a semi-empirical model to predict the viscosity of light hydrocarbon mixtures which is based on the kinetic and intermolecular

contributions to viscosity. The model is presented as a function of temperature, T, and density, ρ, as follows,

$$\eta = K(T,M)\ \mathrm{Exp}[X(T,M)\rho^{y(T,M)}] \tag{2.1.25}$$

where

$$K(T,M) = \frac{A_1+A_2M^q)T^{1.5}}{A_3+A_4M^r+T} \tag{2.1.26}$$

$$X(T,M) = A_5 + A_6/T + A_7M^P \tag{2.1.27}$$

$$y(T,M) = A_8 + A_9\ X(T,M) \tag{2.1.28}$$

P, q and r are taken to be unity, M is the molecular weight and the set of A's are constants determined from experimental data and given in reference (66). By using a linear mixing rule for the molecular weight, equations (2.1.25) through (2.1.28) were extended to predict mixture viscosity. It should be noticed that in the limit when the density goes to zero, equation (2.1.25) reduces to,

$$\eta = \kappa(T,M) \tag{2.1.29}$$

which is the viscosity of the mixture in the dilute case.

2.1.2 Dense Gas And Liquid Mixtures

The theory of transport in dense gas and liquid mixtures is much less complete than the theory of dilute gas transport theory. For this reason, correlations of dense gas and liquid

viscosity are usually empirical. For nonpolar mixtures as in the dilute gas mixture case, the literature has many methods which are intended to predict the viscosity in this range, but probably the most used method is that of Dean and Stiel (21). In the Dean and Stiel correlation, the mixture viscosity, η_m, is represented as a function of the pseudo-reduced mixture density, ρ_{rm}, and the mixture viscosity in the dilute state, η_m^o, as follows,

$$(\eta_m - \eta_m^o)\xi = 1.08\ [\mathrm{Exp}(1.43\rho_{rm}) - \mathrm{Exp}(-1.111\rho_{rm}^{1.858})] \quad (2.1.30)$$

where

$$\rho_{rm} = \rho_m/\rho_{cm} \quad (2.1.31)$$

$$\xi = T_{cm}^{1/6}/\left(\sum_{i=1}^{n} x_i M_i\right)^{1/2} P_{cm}^{2/3} \quad (2.1.32)$$

where ρ_{cm} is the pseudocritical density of the mixture, $\frac{\text{g-mole}}{\text{cc}}$, P_{cm} is the pseudocritical pressure of mixture, T_{cm} is the pseudocritical temperature of mixture, x_i is the mole fraction of component i, and M_i is the molecular weight of component i. Dean and Stiel recommended the mixing rules by Prausnitz and Gunn (98) to estimate the pseudocritical constants.

$$T_{cm} = \sum_{i=1}^{n} x_i T_{ci} \quad (2.1.33)$$

$$V_{cm} = \sum_{i=1}^{n} x_i V_{ci} \quad (2.1.34)$$

$$Z_{cm} = \sum_{i=1}^{n} x_i Z_{ci} \tag{2.1.35}$$

$$P_{cm} = \frac{Z_{cm} RT_{cm}}{V_{cm}} \tag{2.1.36}$$

where T_{ci} is the critical temperature of component i, V_{ci} is the critical volume of component i, Z_{ci} is the compressibility factor of component i, R is the gas constant and n is the number of mixture components.

Even though equation (2.1.30) is intended to predict the viscosity of dense nonpolar mixtures, it has been shown that it can also be applied to dense polar mixtures with slightly larger errors than in the nonpolar case. The reason for applying this correlation to polar mixtures is the lack of a good correlation in the literature which takes into considerations the effects of polar forces on viscosity.

It should be noted that any corresponding states correlation for the viscosity can be used for mixture viscosity calculations using the conformal methods. This approach is discussed in the next chapter.

Same mixture viscosity correlations apply only to the liquid phase. The correlation for binary liquid mixtures of McAllister (81) is based on Eyring's theory of absolute reaction rates. Upon the assumption that free energies of activation for the viscosity of liquid mixtures is being additive on a mole fraction basis, McAllister proposed the

following correlation to predict the kinematic viscosity of liquid mixtures as a function of mole fractions, x_i, and the pure component kinematic viscosities, ν_i,

$$\begin{aligned}\ln \nu_m = {} & x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} \\ & + x_1^3 \ln \nu_2 - \ln[x_1 + x_2 \frac{M_2}{M_1}] \\ & + 3x_1^2 x_2 \ln[(2+\frac{M_2}{M_1})/3] \\ & + 3x_1 x_2^2 \ln[(1+\frac{2M_2}{M_1})/3] \\ & + x_2^3 \ln[\frac{M_2}{M_1}] \end{aligned} \qquad (2.1.37)$$

In this relation, ν is the kinematic viscosity η/ρ, in Centistokes, M_1 and M_2 are the molecular weights of components 1 and 2, and x_1 and x_2 are the mole fractions of components 1 and 2, respectively. The terms ν_{12} and ν_{21} in equation (2.1.37), which are defined as the interaction kinematic viscosities, can be determined from the following relation

$$\nu_{12} = \frac{hN}{M_{12}} \operatorname{Exp}(\frac{\Delta G_{12}}{RT}) \qquad (2.1.38)$$

since

$$\Delta G = \Delta H - T\Delta S \qquad (2.1.39)$$

equation (2.1.38) can be written as,

$$\nu_{12} = \frac{hN}{M_{12}} \operatorname{Exp}(-\frac{\Delta S_{12}}{R}) \operatorname{Exp}(\frac{\Delta H_{12}}{RT}) \qquad (2.1.40)$$

where ΔG is the free energy of activation for viscosity in $\frac{Cal}{g\text{-}mole}$, ΔS is the entropy of activation for viscosity in $\frac{Cal}{g\text{-}mole\ ^{o}K}$, ΔH is the enthalpy of activation for viscosity in $\frac{Cal}{g\text{-}mole}$, N is Avogadro's number, h is Plank's constant (6.624×10^{-27} erg-sec/molecule), and M_{12} is an average molecular weight defined as,

$$M_{12} = \frac{2M_1+M_2}{3} \tag{2.1.41}$$

The definition of M_{12} is peculiar, but occurs because ΔG_{12} is based on the interaction between two molecules of type 1 and one molecule of type 2. Similar expressions can be written for ν_{21}, ν_1 and ν_2 as those of ν_{12}. This approach requires the availability of one of the following items of information,

1. ΔG_1, ΔG_2, ΔG_{12} and ΔG_{21} must be known in order to estimate the parameters needed in equation (2.1.37).

2. The pure kinematic viscosities and the mixture kinematic viscosities must be known at two different temperatures in order to estimate ν_{12} and ν_{21}. Once ν_{12} and ν_{21} are estimated, the mixture kinematic viscosity can be predicted at any other temperatures. And once the mixture kinematic viscosity is estimated, the absolute mixture viscosity can be obtained provided that the liquid mixture density is available.

It should be noted that the use of kinematic viscosity in this correlation and some other correlations for liquid mixture viscosity instead of absolute viscosity is mainly

to avoid quantities such as volume fractions or volume changes on mixing which are not always known quantities.

Kalidas and Laddah extended the McAllister equation to ternary mixtures (58). Their expression is similar to that of McAllister for binary mixtures but has terms added to account for the third component in the system.

Many simple liquid viscosity correlations are presented in the literature and can be generalized in the following form, (98),

$$f(\eta_m) = \sum_{i=1}^{n} x_i f(\eta_i) \qquad (2.1.42)$$

in which $f(\eta)$ can bave such forms as η, $\ln \eta$, or $1/\eta$ and x_i can be the mole fraction, mass fraction or volume fractions. This simplistic approach, of course, will not produce accurate predictions because it does not take into consideration unlike molecular interactions. McAllister's equation probably is the most accurate method strictly for liquid mixtures that is available in the literature. The range of the McAllister equation is not limited to nonpolar liquid mixtures; it also applies to polar mixtures and mixtures with association forces.

2.2 THERMAL CONDUCTIVITY

2.2.1 Dilute Gas Mixtures

The Chapman-Enskog theory produce the following relation for thermal conductivity under the same assumptions used to derive the viscosity relation of equation (2.1.1),

$$\lambda = \frac{15}{4} \frac{R}{M} \eta \qquad (2.2.1)$$

$$= \frac{75}{64} \frac{R}{\pi} \frac{(\frac{\pi RT}{M})^{\frac{3}{2}}}{\sigma^2 \Omega_v} \qquad (2.2.2)$$

$$= \frac{19.891 \times 10^{-5} \, (T/M)^{\frac{1}{2}}}{\sigma^2 \Omega_v} \qquad (2.2.3)$$

where Ω_v is the collision integral. M is the molecular weight, T is the absolute temperature, and σ is the characteristic distance defined as the distance r at zero potential.

As for viscosity, the Chapman-Enskog theory is seldom used for mixtures. However, the literature contains many methods for estimating the thermal conductivity of the dilute gas mixtures. Most of those methods are empirical, and many reduce to the Wassiljewa equation. This equation was proposed in 1904 (129) by Wassiljewa and it is purely empirical. The form of the Wassiljewa equation is anologous to equation (2.1.4) for mixture viscosity,

$$\lambda_m = \sum_{i=1}^{n} \frac{x_i \lambda_i}{\sum_{j=1}^{n} x_j A_{ij}} \qquad (2.2.4)$$

where λ_m is the mixture thermal conductivity, λ_i is the thermal conductivity of pure component i, x_i is the mole fraction of component i, and A_{ij} is an interaction parameter which is as ϕ_{ij} for mixture viscosity is closely related to the diffusion coefficient D_{ij}. The parameter A_{ij} has been the subject of many investigations and many expressions have been proposed in the literature. Some of those expressions will be discussed in the following paragraphs.

a. Mason and Saxena Model

Mason and Saxena (50,98) proposed an expression for A_{ij} which is derived from the rigorous kinetic theory,

$$A_{ij} = \frac{1.065}{2\sqrt{2}} \left(1 + \frac{M_i}{M_j}\right)^{-\frac{1}{2}} \left[1+\left(\frac{\lambda_i^o}{\lambda_j^o}\right)^{\frac{1}{2}} \left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}\right]^2 \qquad (2.2.5)$$

where M_i is the molecular weight of component i and λ_i^o is the monatomic value of the thermal conductivity, or the value of thermal conductivity when all internal degrees of freedom are frozen. The monatomic conductivities λ_i^o and λ_j^o are related to the viscosities η_i and η_j from the kinetic theory as follows,

$$\frac{\lambda_i^o}{\lambda_j^o} = \left(\frac{\eta_i}{\eta_j}\right)\left(\frac{M_i}{M_j}\right) \qquad (2.2.6)$$

so that if η_i and η_j are known, then the ratio $\frac{\lambda_i^o}{\lambda_j^o}$ can be computed via equation (2.2.6). If equation (2.2.6) is substituted into equation (2.2.5), an expression similar to equation (2.1.7) will result, which means that the Wilke's interaction parameter for ϕ_{ij} also can be applied to thermal conductivity and equation (2.1.4) can be used for thermal conductivity by just replacing η by λ in that equation. This conclusion should be taken as an approximation only since momentum and energy transfers take place with different molecular interactions.

If viscosities are not available, Mason and Saxena proposed a model which is based on the Euken factor, E_i,

$$\lambda_i^o = \lambda_i / E_i \qquad (2.2.7)$$

The Euken factor can be estimated using the formula below recommended by Hirschfelder (50),

$$\begin{aligned} E_i &= 0.115 + 0.354(C_p/R) \\ &= 0.115 + 0.354\left(\frac{\gamma}{\gamma-1}\right) \end{aligned} \qquad (2.2.8)$$

where C_p is the molar heat capacity at constant pressure, γ is the ratio C_p/C_v, C_v is the molar heat capacity at constant volume, and R is the ideal gas constant.

b. Lindsay And Bromely Model

An expression for A_{ij} which is based on the Sutherland potential model for viscosity was proposed by Lindsay and

Bromely (72),

$$A_{ij} = \tfrac{1}{4}\{1 + [\frac{\eta_i}{\eta_j}(\frac{M_j}{M_i})^{\frac{3}{4}} \frac{(1 + \frac{S_i}{T})}{(1 + S_j/T)}]^{\frac{1}{2}}\} \frac{(1 + \frac{S_{ij}}{T}}{(1 + \frac{S_i}{T})} \qquad (2.2.9)$$

where S_i is the Sutherland constant defined as,

$$S = 1.5\ T_b \qquad (2.2.10)$$

where T_b is the boiling point at one atmosphere. Equation (2.2.10) holds reasonably for all fluid except hydrogen, deterium and helium where the value of S = 79 ^{o}K. The value of S_{ij} is defined as,

$$S_{ij} = C(S_i S_j)^{\frac{1}{2}} \qquad (2.2.11)$$

where C is a binary interaction parameter taken to be unity for nonpolar mixtures and 0.733 for mixtures containing at least one polar constituent. Other values for C have been recommended in the literature and they vary according to authors but Bennett and Vines (8) concluded that C has to be adjusted individually for each system especially when the mixture is polar-nonpolar.

Other investigators have proposed different models for the coefficient of interaction, A_{ij}, of the Wassiljewa equation and some of those are found in the following references (11,27,40,41,42,59,60,75,80).

Other methods for estimating dilute gas thermal conductivity are available in the literature which are not derived or related to the Wassiljewa equation. Among those methods is the simple formula proposed by Ulybin (126) which is based on the molecular kinetic theory. The Ulybin equation is dependent on the pure component thermal conductivity, λ_i, molecular weight, M_i, and the mixture mole (volume) fractions, x_i

$$\lambda_m = \frac{\sum_{i=1}^{n} x_i / M_i^{\frac{1}{2}}}{\left[\sum_{i=1}^{n} \frac{x_i}{M_i^{\frac{1}{4}} \lambda_i^{\frac{1}{2}}}\right]^2} \qquad (2.2.12)$$

Ulybin compared his equation with that of Mason and Saxena for both monatomic and polyatomic mixture and the results obtained by his equation were comparable.

Brokaw (10) introduced an empirical equation which he found to produce compatable results to the Wassiljewa equations for binary nonpolar mistures. Brokaw's equation is,

$$\lambda_m = a\,\lambda_{SM} + (1-a)\lambda_{RM} \qquad (2.2.13)$$

and

$$\lambda_{SM} = x_1\lambda_1 + x_2\lambda_2 \qquad (2.2.14)$$

$$\lambda_{RM} = \frac{x_1}{\lambda_1} + \frac{x_2}{\lambda_2} \qquad (2.2.15)$$

where λ_{SM} is the simple molar mixing of the thermal conductivity of the pure components, λ_i, λ_{RM} is reciprocal molar mixing,

x_i is the mole fraction of component i and a is a numerical parameter given by Brokaw (10) as a function of mixture composition.

If the thermal conductivity of the mixture is available at a temperature T_1 along with the pure component thermal conductivities at T_1 and T_2, then an equation proposed by Ulybin et al (125) can be used to predict the mixture thermal conductivity at T_2

$$\lambda_m(T_2) = \lambda_m(T_1) \sum_{i=1}^{n} \frac{x_i \lambda_i(T_2)}{\lambda_i(T_1)} \qquad (2.2.16)$$

Saxena and Gupta (104) tested equation (2.2.16) for binary, ternary and quaternary mixtures of nonpolar gases and the results were compatable to other correlations.

2.2.2 Dense Gas And Liquid Mixtures

Gilmore and Comings (39) tested the Lindsay-Bromely method, equation (2.2.9) which was orginally proposed for dilute gas mixtures on several nonpolar dense gaseous mixtures, such as CO_2-N_2, CO_2-N_2H_6 and N_2-C_2H_6 and found very good agreement with the experimental data. They concluded that his method is also applicable to nonpolar dense gaseous mixtures.

Stiel and Thodos (115) proposed a set of equations for the prediction of pure thermal conductivity, λ_i, from

dimensional analysis. The equations involved are listed below,

$$(\lambda_i - \lambda_i^o)F_i Z_{ci}^5 = 14.00[\mathrm{Exp}(-0.535\rho_{Ri}) - 1] \times 10^{-8},$$
$$\rho_{Ri} < 0.5 \qquad (2.2.17)$$

$$(\lambda_i - \lambda_i^o)F_i Z_{ci}^5 = 13.10[\mathrm{Exp}(0.67\rho_{Ri}) - 1.069] \times 10^{-8},$$
$$0.5 < \rho_{Ri} < 2.0 \qquad (2.2.18)$$

$$(\lambda_i - \lambda_i^o)\ F_i Z_{ci}^5 = 2.976[\mathrm{Esp}(1.155\rho_{Ri}) - 2.016] \times 10^{-8},$$
$$2.0 < \rho_{Ri} < 2.8 \qquad (2.2.19)$$

where $\rho_{Ri} = \frac{\rho_i}{\rho_{ci}} = \frac{V_{ci}}{V_i}$, ρ_i is the density of pure component i, ρ_{ci} is the critical density of component i, V_{ci} is the critical volume of component i, V is the volume of pure component i,

$$F_i = T_{ci}^{\frac{1}{6}}\ M_i^{\frac{1}{2}}/P_{ci}^{\frac{2}{3}} \qquad (2.2.20)$$

T_{ci} is the critical temperature of component i, M_i is the molecular weight of component i, P_{ci} is the critical pressure of component i, Z_{ci} is the critical compressibility of component i,

$$Z_{ci} = P_{ci}V_{ci}/RT_{ci} \qquad (2.2.21)$$

and R is the gas constant.

Reid, et al (98) extended this equation to predict the mixture thermal conductivity of nonpolar dense gaseous mixtures by using the modified Prausnitz and Gunn combining rules, equations (2.1.33) through (2.1.36) to calculate the pseudocritical properties of the mixture. Satisfactory results were obtained when this method was used (98).

Summaries of methods for estimating the thermal conductivity of liquid mixtures are found in references (56, 57,98). It was found that the molar averages for liquid mixture thermal conductivity values are higher generally than the experimental values; therefore, weight fractions were recommended instead. A few methods will be briefly discussed in the following paragraphs.

a. NEL Equation

This equation is only good for binary liquid mixtures and generally produces very good results (56,98),

$$\frac{\lambda_m-\lambda_1}{\lambda_2-\lambda_1} = \alpha\omega_2^{\frac{3}{2}} + \omega_2(1-\alpha) \qquad (2.2.22)$$

where ω_2 is the weight fraction of component 2, and α is a constant which depends on the particular mixture under investigation. The constant α can be taken as zero in many cases with only a slight increase in the error of prediction.

b. Filipov Equation

This equation is one of the most accurate liquid thermal

conductivity correlations available (56,98) even though it is completely empirical,

$$\frac{\lambda_m - \lambda_1}{\lambda_2 - \lambda_1} = C\omega_2^2 + \omega_2(1-C) \qquad (2.2.23)$$

where C is a constant which is unique for the particular mixtures under investigation. The value of C can be taken to be 0.72 if it cannot be determined from experimental data. The accuracy of this equation is similar to that of the NEL equation.

c. Vernart Equation

For binary organic liquid mixtures, Venart (127) proposed the following model,

$$\lambda_m = [\lambda_1 + (\lambda_2 - \lambda_1)x_2][1 - x_1x_2 \frac{\Delta E}{kT}] \qquad (2.2.24)$$

where x_2 is the mole fraction of component 2, ΔE is a constant (determined from data) called the interchange energy which represents the increase in energy that one molecule acquires when it exchanges its own neighbors for neighbors of another kind and k is the Boltzmann's constant. Jamieson (56) compared this equation with experimental data and found out that it predicted thermal conductivity with slightly lower accuracy than the NEL equation.

d. Jordon-Coates Equation

Shroff (105) recommended the Jordon-Coates equation after comparing it with experimental data. This equation

is only applicable to binary liquid mixtures,

$$\ln \lambda_m = \omega_1 \ln \lambda_1 + \omega_2 \ln \lambda_2 + \omega_1\omega_2 \ln J \qquad (2.2.25)$$

and

$$J = \text{Exp}[|\lambda_2 - \lambda_1|] - 0.5(\lambda_2 - \lambda_1) \qquad (2.2.26)$$

Equations (2.2.25) and (2.2.26) in this form must be used with engineering units of Btu, hr, ft, and ^{o}F.

e. Lee Equation

All the previous liquid mixture thermal conductivity equations are only applicable to binary mixtures. It was not until 1976 that a method was proposed to predict multicomponent liquid mixture thermal conductivity with good accuracy. Lee (71) proposed the following method for multicomponent liquid mixtures,

$$\lambda_m = \sum_{i=1}^{n} \sum_{j=1}^{n} \phi_i \phi_j \lambda_{ij} \qquad (2.2.27)$$

where

$$\lambda_{ij} = 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1} \qquad (2.2.28)$$

and

$$\phi_i = \frac{x_i V_i}{\sum_{j=1}^{n} x_j V_j} \qquad (2.2.29)$$

where V_i is the molar volume of component i, x_i is the mole fraction of component i, and ϕ_i is the volume fraction of component i.

Equation (2.2.27) was tested by Lee (71) for many binary systems including systems with polar-nonpolar, polar-polar

and association forces. The predictions were as accurate as those using the NEL and Filipov equations and in many cases much better results were obtained.

The above mentioned equations are by no means the only methods available in the literature for predicting the thermal conductivities of liquid mixtures, but might be taken as representative of the simplest accurate methods for wide ranges of liquid mixture. Other methods are listed in the following references (26,45,98).

It should be noted that any corresponding states correlation for the thermal conductivity can be used for mixture thermal conductivity calculations using the conformal solution methods. This approach is discussed in the next chapter.

2.3 Experimental Data

Experimental data are essential in the development of any new correlation in order to determine the correlation applicability and accuracy. In this work the methods presented are applicable to all fluid states, including dilute gas, dense and liquid mixtures for monatomic, polatomic, polar, polar-nonpolar and mixtures with association forces. Therefore, to substantiate this claim a thorough literature survey was performed to obtain experimental data which cover all the ranges mentioned above.

One main obstacle that was faced was the avilability of density values. Since both the viscosity and thermal conductivity correlations used here in are functions of temperature and density. To date, no equation of state (EOS) has been developed to predict the density of polar-polar, polar-nonpolar and associated mixtures. An EOS such as the modified BWR equation (112,113) is capable of predicting the density of nonpolar mixtures with high accuracy; but however, the binary interaction parameters needed in this EOS must be available for each mixture under investigation.

Experimental data for viscosity and thermal conductivity in the dilute gas range were avilable in the literature for many systems but more data are needed for mixtures with association forces, e.g., alcohols, water, and ketones.

In dense gas state, more experimental data are needed for nonpolar mixtures with constituents different in size and shape. Also, mixtures of dense gases with polar forces and association forces are needed.

In the liquid range, the need for data for low temperature mixtures and compressed liquid mixtures is quite high.

In all the mentioned cases above, density values are required along with either transport property data until the time an equation of state is developed to cover all fluid mixtures for all density regions.

In this work, the densities for most of the liquid mixtures were calculated using the Hankinson-Thomson equation (44) unless densities were reported along the experimental transport property data or calculated by the MBWR equation of state.

CHAPTER III

A CORRELATION BASED ON CORRESPONDING STATES THEORY UTILIZING A CONFORMAL SOLUTION MODEL

3.1 Theory

The perturbation theory is used here for the derivation of a corresponding state correlation for prediction of the transport properties of pure and mixture fluids. The importance of the theory stems from the requirement that the perturbation expansion must be made convergent.

If any transport property R, is expanded about a reference system's transport property R_o, the result will be,

$$R = R_o + R_1 + R_2 + R_3 + \ldots \qquad (3.1.1)$$

in which R might be the viscosity, thermal conductivity or diffusion coefficient. The objective of the perturbation theory is to make the terms $R_1 + R_2 + R_3 + \ldots$ rapidly convergent.

To deal with nonpolar as well as polar polyatomic fluids, the Pople theory (94) has proved to be successful in predicting the thermodynamic behavior of fluids. Therefore, the spirit of this approach has been applied for transport property correlation. For a pair of interacting molecules, the potential energy is

$$U_{ij}(\underline{r}_{ij} = U_j(\underline{r}_{ij}) + U_p(\underline{r}_{ij} \qquad (3.1.2)$$

where $\underline{r}_{ij}$ is the vector separation between molecules i and j

and Ω_i and Ω_j are the Euler angles describing the relative orientations of the pair of molecules i and j. U_o represents the isotropic contribution to the potential, which is a function of the molecular separation but not molecular orientation, and U_p represents the anisotropic contribution to the potential, which is a function both of molecular separation and the orientations of the molecules.

Mo and Starling (85) proved that the reduced transport property R* can be written in a form similar to that of equation (3.1.1),

$$R^* = R^*_o + R^*_2 + R^*_3 + \ldots \tag{3.1.3}$$

Now, consider a polyatomic fluid (polar or nonpolar); the potential energy can be described as

$$U_{ij} = U^o_{ij} + U^P_{ij} \tag{3.1.4}$$

where

$$U^o_{ij} = \varepsilon_{ij}\, f_o\left(\frac{r_{ij}}{\sigma_{ij}}\right) \tag{3.1.5}$$

$$U^P_{ij} = \sum_m \varepsilon^m_{ij}\, f^m_p\left(\frac{r_{ij}}{\sigma_{ij}}\right)\, \gamma^m_{ij}\, (\Omega_i \Omega_j) \tag{3.1.6}$$

The superscript in equation (3.1.6) represents the various types of anisotropic molecular interactions which contribute to the system's potential such as the dipole-dipole, dipole-quadrupole, dipole-induced dipole, etc.

The dipole-dipole interaction term is represented by the

relation,

$$U_{ij}^{\mu\mu} = \frac{\mu_i\mu_j}{r_{ij}^3} (S_iS_jC - 2C_iC_j) \tag{3.1.7}$$

where $S_i = \sin\theta_i$, $C_i = \cos\theta_i$, $C = \cos\psi_{ij}$, θ_i and θ_j are the polar angles, $\psi_{ij} = \psi_i - \psi_j$ which is the azimuthal angle representing the oriented dipoles at the separation distance r_{ij} and μ_i and μ_j are the dipole moments of molecules i and j.

Thus, the dipole-dipole interaction term in equation (3.1.6) is represented by the relation,

$$U_{ij}^{\mu\mu} = \varepsilon_{ij}^{\mu\mu} f_{ij}^{\mu\mu} \left(\frac{r_{ij}}{\sigma_{ij}}\right) \gamma_{ij}^{\mu\mu} (\Omega_i\Omega_j) \tag{3.1.8}$$

where

$$\varepsilon_{ij}^{\mu\mu} = \mu_i\mu_j/\sigma_{ij}^3 \tag{3.1.9}$$

$$\gamma_{ij}^{\mu\mu} (\Omega_i\Omega_j) = S_iS_jC - 2C_iC_j \tag{3.1.10}$$

$$f_{ij}^{\mu\mu} = (\sigma_{ij}/r_{ij})^3 \tag{3.1.11}$$

and

$$\Omega_i = \theta_i\psi_i \tag{3.1.12}$$

The term representing the dipole-induced dipole is given by the relation,

$$U_{ij}^{\mu\alpha} = \frac{\mu_i^2\alpha_j}{\sigma_{ij}^6} (3C_i^2 + 1) \tag{3.1.13}$$

where α_j is the polarizability of molecule j. Thus the dipole-induced dipole interaction term is represented in equation (3.1.6) by,

$$U_{ij}^{\mu\alpha} = \epsilon_{ij}^{\mu\alpha} f_{ij}^{\mu\alpha}(\frac{r_{ij}}{\sigma_{ij}}) \gamma_{ij}^{\mu\alpha} (\Omega_i\Omega_j) \tag{3.1.14}$$

where

$$\epsilon_{ij}^{\mu\alpha} = \mu_i^2\alpha_j/\sigma_{ij}^6 \tag{3.1.15}$$

$$\gamma_{ij}^{\mu\alpha} = (3C_i^2 + 1) \tag{3.1.16}$$

and

$$f_{ij}^{\mu\alpha} = (\sigma_{ij}/r_{ij})^6 \tag{3.1.17}$$

Therefore, using proper representations for all possible molecular interactions, the reduced transport property R^*, to third order in the expansion perturbation can be expressed in the form

$$R^*(T^*,\rho^*) = R_o^*(T^*,\rho^*) + \sum_m \sum_n \frac{\epsilon^m\epsilon^n}{\epsilon^2} F_2^{mn}(T^*,\rho^*) + \sum\sum\sum \frac{\epsilon^\rho\epsilon^m\epsilon^n}{\epsilon^3} F_3^{lmn}(T^*,\rho^*) \tag{3.1.18}$$

The task of evaluating F_2 and F_3 mathematically is extremely difficult. To avoid this difficulty, a multiparameter corresponding states approach will yield expressions for those functions. In earlier research at the University of

Oklahoma, that task was performed and generalized multi-parameter corresponding states correlations for viscosity and thermal conductivity were developed (19).

Extension of the pure transport perturbation theory expansion to mixtures is similar in methodology, but the mixture composition must be included. Thus, the perturbation expansion to second order is given by,

$$R^*(T^*,\rho^*) = R_o^*(T^*, {}^*) + \sum_i \sum_j x_i x_j R_2^*(T^*,\rho^*) \qquad (3.1.19)$$

where

$$R_2^*(T^*,\rho^*) = \sum_m \sum_n \varepsilon_{ij}^m \; \varepsilon_{ij}^n \; \sigma_{ij}^{mn} \; G_2^{mn} \; (T_{ij}^*,\rho_{ij}^*) \qquad (3.1.20)$$

The function G_2 in equation (3.1.20) and the function F_2 of equation (3.1.18) are related by the relation,

$$G_2^{mn} = \varepsilon_{ij}^2 \; F_2^{mn}/\sigma_{ij}^3 \qquad (3.1.21)$$

and x_i is the mole fraction of component i in the mixture.

As in the pure fluid case, the task of evaluating F_2 and G_2 is mathematically very difficult. Therefore, a conformal solution model approach will be utilized herein.

Consider a mixture containing N_α molecules of components a,b,c,... in a volume V at temperature T. Assuming that all mixture components are conformal which means that they all obey

the same intermolecular pair potential. Therefore, the potential can be written in a similar form to those of equations (3.1.4), (3.1.5) and (3.1.6) combined together,

$$U_{ij}(\underline{r}_{ij},\Omega_i\Omega_j) = \varepsilon_{ij} f_o(\frac{r_{ij}}{\sigma_{ij}}) + \sum_m^m \varepsilon_{ij} f_p^m(\frac{r_{ij}}{\sigma_{ij}}) \gamma_{ij}^m(\Omega_i\Omega_j) \qquad (3.1.22)$$

where the superscript m refers to the type of anisotropic molecular interaction.

Now, consider a reference mixture of the same N_α molecules of compounds a,b,c... at the same V and T as the real mixture but in this case all components have the same molecular mass m_x and the same interaction parameters, σ_x, ε_x and γ_x. Therefore, the potential is given by,

$$U_x(\underline{r}_{ij},\Omega_i\Omega_j) = \varepsilon_x f(\frac{r_{ij}}{\sigma_x}) + \sum_m \varepsilon_x^m f_p^m(\frac{r_{ij}}{\sigma_x}) \gamma_x^m(\Omega_i\Omega_j) \qquad (3.1.23)$$

The transport property of the mixture, R_m, can now be expanded about the transport property of the reference mixture using as expansion parameters combinations of the potential parameters and the reduced molecular masses m_{ij}^*. The reduced molecular mass for a molecule pair, m_{ij}^*, is defined to be

$$m_{ij}^* = m_i m_j/(m_i + m_j) \qquad (3.1.24)$$

where m_i and m_j are the molecular masses of components i and j in the mixture.

Let the following parameters represent the given combinations of factors of characterization parameters, the perturbation expansion (113),

$$a_{ij} = \gamma_{ij}^{e}\varepsilon_{ij}^{f}\sigma_{ij}^{g}m_{ij}^{*h} \qquad b_{ij} = \gamma_{ij}^{k}\varepsilon_{ij}^{\ell}\sigma_{ij}^{m}m_{ij}^{*n}$$

$$c_{ij} = \gamma_{ij}^{o}\varepsilon_{ij}^{p}\sigma_{ij}^{q}m_{ij}^{*r} \qquad d_{ij} = \gamma_{ij}^{s}\varepsilon_{ij}^{t}\sigma_{ij}^{y}m_{ij}^{*v}$$

where the exponents e through v are left unspecified for the time being. Thus, the expansion of the mixture transport property R, to first order is,

$$R = R_x + \sum_i \sum_j \left(\frac{\partial R}{\partial a_{ij}}\right)_x (a_{ij} - a_x) + \sum_i \sum_j \left(\frac{\partial R}{\partial b_{ij}}\right)_x (b_{ij} - b_x)$$

$$+ \sum_i \sum_j \left(\frac{\partial R}{\partial c_{ij}}\right)_x (C_{ij} - C_x) + \sum_i \sum_j \left(\frac{\partial R}{\partial d_{ij}}\right)_x (d_{ij} - d_x)$$

$$+ \text{higher order terms} \qquad (3.1.25)$$

where a_x, b_x, c_x, d_x are the values of a_{ij}, b_{ij}, c_{ij}, d_{ij} when γ_{ij}, ε_{ij}, σ_{ij}, m_{ij}^* equal γ_x, ε_x, σ_x, m_x^*, respectively.

It is assumed that higher order terms made very little contribution to the transport properties. This is accomplished exactly for the first order perturbation terms by selecting a_x, b_x, c_x, d_x to annul those terms. This reduces equation (3.1.25) to the simple relation,

$$R_m = R_x \tag{3.1.26}$$

Without specifying the exponents, the following relations achieves this objective,

$$\gamma_x^e \varepsilon_x^f \sigma_x^f m_x^{*h} = \sum_i \sum_j x_i x_j \gamma_{ij}^e \varepsilon_{ij}^f \sigma_{ij}^g m_{ij}^{*h} \tag{3.1.27}$$

$$\gamma_x^k \varepsilon_x^l \sigma_x^m m_x^{*n} = \sum_i \sum_j x_i x_j \gamma_{ij}^k \varepsilon_{ij}^\ell \sigma_{ij}^m m_{ij}^{*n} \tag{3.1.28}$$

$$\gamma_x^o \varepsilon_x^p \sigma_x^q m_x^{*r} = \sum_i \sum_j x_i x_j \gamma_{ij}^o \varepsilon_{ij}^p \sigma_{ij}^q m_{ij}^{*r} \tag{3.1.29}$$

$$\gamma_x^s \varepsilon_x^t \sigma_x^y m_x^{*v} = \sum_i \sum_j x_i x_j \gamma_{ij}^s \varepsilon_{ij}^t \sigma_{ij}^y m_{ij}^{*v} \tag{3.1.30}$$

These equations are commonly referred to as mixing rules for γ_x, ε_x, σ_x, m_x^*.

The choices for the exponents in equations (3.1.27) through (3.1.30) are arbitrary but at the same time the accuracies of prediction of the particular transport property, whether the mixture viscosity, η, or thermal conductivity, λ, are sensitive to the exponent choices. No matter what the exponents are, equation (3.1.25) will reduce to equation (3.1.26), when higher order terms are ignored. The choices for exponents are discussed in the next section of this chapter.

3.2 Mixing Rules

A. The Modified Van Der Waals One Fluid Mixing Rules

The well-known Van der Waals one fluid mixing rules for σ_x and ε_x have been successful in predicting the thermodynamic

behavior of isotropic fluid mixtures (70,86,96,108). Therefore, for σ_x and ε_x in this work, these mixing rules are adopted (other mixing rules also are used, as noted subsequently). This means that equations (3.1.27) and (3.1.28) will reduce to,

$$\sigma_x^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \tag{3.2.1}$$

$$\varepsilon_x \sigma_x^3 = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \tag{3.2.2}$$

This corresponds to the following values for the exponents in equations (3.1.27) and (3.1.28), $e = f = h = k = n = o$, $g = m = 3$ and $\ell = 1$.

The parameter c_{ij} which embodies all possible anisotropic contributions such as the shape effects represented by the Pitzer acentric factor, ω_{ij}, the dipole-dipole interaction, the dipole-induced dipole interaction and hydrogen bonding represented by the association parameter κ_{ij}, must be broken into separate contributions and each one represented by an individual mixing rule. The mixing rule for the Pitzer acentric factor is adopted from the successful thermodynamic application (69,113) for polyatomic nonpolar mixutres. The mixing rule is given as,

$$\omega_x \varepsilon_x^2 \sigma_x^3 = \sum_i \sum_j x_i x_j \omega_{ij} \varepsilon_{ij}^2 \sigma_{ij}^3 \tag{3.2.3}$$

The dipole-dipole interaction is obtained from the perturbation theory discussed earlier in Section 3.1. For the dipole-dipole interaction, the mixing rule is

$$\mu_x^4 \sigma_x^{-3} = \sum_i \sum_j x_i x_j \mu_i^2 \mu_j^2 \sigma_{ij}^{-3} \qquad (3.2.4)$$

where μ_i^* is the dipole moment of component i in the mixture, in debyes.

The perturbation theory does not account for the association contribution to the potential energy, thus to represent the association effect given by κ_{ij}, the following mixing rule was used

$$\kappa_x = \sum_i \sum_j x_i x_j \kappa_{ij} \qquad (3.2.5)$$

Finally, the exponents for the last parameter d_{ij}, which will provide the reference system reduced mass, m_x^*, must be determined. The kinetic contribution to the transport properties is dominant in the gas phase while collisional forces are the main contributors in the dense gas and liquid phases. These phenomena suggest the use of differing values for the reduced mass in calculating the kinetic contribution, and the potential contribution to the reduced property. Therefore, two different masses will be used to represent the kinetic mass m_{xk}^* and the potential mass m_{xp}^*. Mo and Gubbins (84) discussed several mixing rule alternatives for the reduced mass and the following mixing rules for m_{xk}^* and m_{xp}^* yield the best results, according to studies performed in the present research,

$$\varepsilon_x \sigma_x^2 \, (m^*_{xk})^{\frac{1}{2}} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^2 (m^*_{ij})^{\frac{1}{2}} \qquad (3.2.6)$$

$$\varepsilon_x \sigma_x^4 \, (m^*_{xp})^{\frac{1}{2}} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^4 (m^*_{ij})^{\frac{1}{2}} \qquad (3.2.7)$$

the set of mixing rules which results are referred to herein as the modified Van der Waals mixing rules, they are summarized in Table 3.2.1.

It should be noted that according to studies performed in this research that equation (3.2.4) was adequate in calculating the dipole moment of the reference hypothetical fluid, μ_x for both polar-polar and polar-nonpolar mixtures.

B. The Semi-Empirical Exponent Mixing Rules

The exponents of equations (3.1.27), (3.1.28) and a part of equation (3.1.29) for the acentric factor ω, have been determined empirically by using vapor-liquid equilibrium experimental data for eight binary mixture systems and the results have been report by Lee, Lee and Starling (69). These new mixing rules were also used in this work along with other mixing rules for the remaining contributions which are not considered by Lee, Lee and Starling. The mixing rules are,

$$\sigma_x^{4.5} = \sum_i \sum_j x_i x_j \sigma_{ij}^{4.5} \qquad (3.2.8)$$

$$\varepsilon_x \sigma_x^{4.5} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^{4.5} \qquad (3.2.9)$$

$$\omega_x \sigma_x^{3.5} = \sum_i \sum_j x_i x_j \omega_{ij} \sigma_{ij}^{3.5} \qquad (3.2.10)$$

Table 3.2.1 Summary of Mixing Rules

A. The Modified Van Der Waals Mixing Rules:

$$\sigma_x^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3$$

$$\varepsilon_x \sigma_x^3 = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3$$

$$\omega_x \varepsilon_x^2 \sigma_x^3 = \sum_i \sum_j x_i x_j \omega_{ij} \varepsilon_{ij}^2 \sigma_{ij}^3$$

$$\mu_x^4 \sigma_x^{-3} = \sum_i \sum_j x_i x_j \mu_i^2 \mu_j^2 \sigma_{ij}^{-3}$$

$$\kappa_x = \sum_i \sum_j x_i x_j \kappa_{ij}$$

$$\varepsilon_x \sigma_x^2 m_{xk}^{*1/2} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^2 m_{ij}^{*1/2}$$

$$\varepsilon_x \sigma_x^4 m_{xp}^{*1/2} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^4 m_{ij}^{*1/2}$$

B. The Semi-Empirical Exponent Mixing Rules

$$\sigma_x^{4.5} = \sum_i \sum_j x_i x_j \sigma_{ij}^{4.5}$$

$$\varepsilon_x \sigma_x^{4.5} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^{4.5}$$

$$\omega_x \sigma_x^{3.5} = \sum_i \sum_j x_i x_j \omega_{ij} \sigma_{ij}^{3.5}$$

Table 3.2.1 (Continued)

$$\mu_x^4\sigma_x^{-3} = \sum_i \sum_j x_i x_j \mu_i^2 \mu_j^2 \sigma_{ij}^{-3}$$

$$\kappa_x = \sum_i \sum_j x_i x_j \kappa_{ij}$$

$$\varepsilon_x \sigma_x^2 \, m_{xk}^{*-\frac{1}{2}} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^2 \, m_{ij}^{*-\frac{1}{2}}$$

$$\varepsilon_x \sigma_x^4 (m_{xp}^*)^{\frac{1}{2}} = \sum_i \sum_j x_i x_j \sigma_{ij}^4 (m_{ij}^*)^{\frac{1}{2}}$$

For the dipole-dipole and the association parameter, the same mixing rules are used as those of the modified van der Waals one fluid mixing rules, namely equations (3.2.4) and (3.2.5).

The mixing rules for the reduced masses which were found to yield the best results when used with the semi-empirical exponent mixing rules are

$$(\varepsilon_x)^{\frac{1}{2}}\sigma_x^2\ (m^*_{xk})^{-\frac{1}{2}} = \sum_i \sum_j x_i x_j (\varepsilon_{ij})^{\frac{1}{2}}\sigma_{ij}\ (m^*_{ij})^{-\frac{1}{2}} \tag{3.2.11}$$

$$\varepsilon_x\sigma_x^4\ (m^*_{xp})^{\frac{1}{2}} = \sum_i \sum_j x_i x_j \varepsilon_{ij}\sigma_{ij}(m^*_{ij})^{-\frac{1}{2}} \tag{3.2.12}$$

The semi-empirical exponent mixing rules also are summarized in Table 3.2.1.

The following combining rules were utilized for the unlike pair interaction parameters σ_{ij}, ε_{ij}, ω_{ij} and κ_{ij} and m^*_{ij},

$$\sigma_{ij} = \xi_{ij}(\sigma_{ii}\sigma_{jj})^{\frac{1}{2}} \tag{3.2.13}$$

$$\varepsilon_{ij} = \zeta_{ij}(\varepsilon_{ii}\varepsilon_{jj})^{\frac{1}{2}} \tag{3.2.14}$$

$$\omega_{ij} = (\omega_{ii} + \omega_{jj})/2 \tag{3.2.15}$$

$$\kappa_{ij} = (\kappa_{ii}\kappa_{jj})^{\frac{1}{2}} \tag{3.2.16}$$

$$m^*_{ij} = m_{ii}m_{jj}/(m_{ii} + m_{jj}) \tag{3.2.17}$$

Unsatisfactory results were produced by using equation (3.2.16) for associated mixtures. Therefore, it was necessary to empirically determine other combining rules for the unlike interaction term κ_{ij}. It was necessary to use differnet combining rules for each transport property and for specific class of associated mixtures. The combining rules for κ_{ij} are

$$\kappa_{ij} = \phi_{ij}\left(\frac{\kappa_{ii} + \kappa_{jj}}{\kappa_{ii}\,\kappa_{jj}}\right) \tag{3.2.18a}$$

or

$$\kappa_{ij} = \phi_{ij}\left(\frac{\kappa_{ii} + \kappa_{jj}}{2}\right) \tag{3.2.18b}$$

Equation (3.2.18a) is used for the viscosity prediction of binary aqueous mixtures and equation (3.2.18b) is used to predict the viscosity of nonwater associated mixtures and the thermal conductivity of all associated binary mixtures.

The binary interaction parameters ξ_{ij} of equation (3.2.13) and ϕ_{ij} of equations (3.2.18a) and (3.2.18b) were generalized for the associated mixtures as a function of the molecular weights of the individual constituents of the binary mixture. The parameter ζ_{ij} was fixed at unity value. The generalized parameters are

$$\xi_{ij} = a + b\left(\frac{M_h}{M_l}\right) \tag{3.2.19}$$

$$\phi_{ij} = c\left(\frac{M_h}{M_l}\right)^d \tag{3.2.20}$$

where $M_h > M_l$, and M is the molecular weight of either component i or j. The parameter a, b, c and d are constants which are subsequently listed according to the following categories.

1. Viscosity:

   A. Aqueous Mixtures:

      a = 1.1212, b = -0.18, c = 0.058 and d = 0.97

for the semiempirical mixing rules (SEE).

      a = 1.11857, b = -0.17, c = 0.055 and d = 0.78

for the modified van der Waals mixing rules (MvdW).

   B. Nonaqueous Associated Mixture:

      a = 0.947765, b = 0.078, c = 0.062 and d = -3.44

for the SEE.

      a = 0.851857, b = 0.185, c = 0.092 and d = -3.98

for the MvdW.

2. Thermal Conductivity:

   A. Aqueous Mixtures:

      a = 1.02547, b = -0.36, c = 0.223 and d = -0.343

for the SEE.

      a = 1.06016, b = -0.41, c = 0.43 and d = 0.55

for the MvdW.

   B. Nonaqueous Associated Mixtures:

      a = 0.906879, b = 0.11, c = 0.026 and d = 2.18

for the SEE.

      a = 0.901061, b = 0.11, c = 0.063 and d = 1.45

for the MvdW.

3.3 Equations of State

Since both the viscosity and thermal conductivity equations used herein are functions of temperature and density, and equation of state is required for the mixiture density determination.

A modified BWR equation of state (BWRS) has been developed by Starling (112,113) for thermodynamic properties predictions nonpolar fluids in all fluid states. The BWRS equation is

$$Z = 1 + [B(1) - \frac{B(2)}{T^*} - \frac{B(3)}{T^{*3}} + \frac{B(4)}{T^{*4}} - \frac{B(11)}{T^{*5}}]\rho^*$$

$$+ [B(5) - \frac{B(6)}{T^*} - \frac{B(10)}{T^{*2}}]\rho^{*2} + [\frac{B(7)}{T^*} + \frac{B(12)}{T^{*2}}]\rho^{*5}$$

$$+ B(8)\ [1 + B(4)\rho^{*2}]\ \frac{\rho^{*2}}{T^{*3}} \exp\ (-B(4)\rho^{*2}) \qquad (3.3.1)$$

where Z is the compressibility factor, $T^* = \frac{kT}{\varepsilon}$ and $\rho^* = \rho\sigma^3$. The parameters B(I), I = 1,2,...12 are generalized using the relation

$$B(I) = B_o(I) + B_a(I), \quad I = 1,2,3...12 \qquad (3.3.2)$$

where $B_o(I)$ and $B_a(I)$ are the isotropic and anisotropic contributions respectively. The parameters B(I) are generalized for nonpolar fluids as functions of the orientation parameter γ (γ is related to the Pitzer acentric factor which is determined

from regression using experimental data) using the relation

$$B(I) = B_o(I) + \gamma B_1(I) \tag{3.3.3}$$

Values of $B_o(I)$ and $B_1(I)$ for I = 1,2,...12 are summarized in Table 3.3.1. The critical temperature T_c and critical density ρ_c were used to estimate the characteristic parameters ε and σ from the relations,

$$\varepsilon = kT_c/1.2593 \tag{3.3.4}$$

$$\sigma^3 = 0.3189/\rho_c \tag{3.3.5}$$

where k is the Boltzmann constant. The relations (3.3.4) and (3.3.5) were determined by McDonald (82) from molecular dynamic simulations of Arogon experimental data.

Equation (3.3.1) is extended to mixtures by using the conformal solution model approach. The modified van der Waals one fluid mixing rules were used to determine the characteristic parameters of the reference hypothetical fluid,

$$\sigma_x^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \tag{3.3.6}$$

$$\varepsilon_x \sigma_x^3 = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \tag{3.3.7}$$

$$\gamma_x \varepsilon_x^2 \sigma_x^3 = \sum_i \sum_j x_i x_j \gamma_{ij} \varepsilon_{ij} \sigma_{ij}^3 \tag{3.3.8}$$

Table 3.3.1 Parameters $B_o(I)$ and $B_1(I)$ For Use With The BWRS Equation (3.3.1)

I	$B_o(I)$	$B_1(I)$
1	1.45907	0.328721
2	4.98813	-2.64399
3	2.20704	11.3293
4	4.86121	0
5	4.59311	2.79979
6	5.06707	10.3901
7	11.4871	10.3730
8	9.22469	20.5388
9	0.0946236	2.76010
10	1.48858	-3.11349
11	0.0152729	0.189147
12	3.51486	0.942596

More accurate mixing rules were recently determined by Starling et al (69) in which the exponents of the mixing rules were obtained from experimental data regression. These so-called semi-empirical exponent mixing rules can be also used determine the mixture density from the BWRS equation of state. The semiempirical exponent mixing rules are

$$\sigma_x^{4.5} = \sum_i \sum_j x_i x_j \sigma_{ij}^{4.5} \tag{3.3.9}$$

$$\varepsilon_x \sigma_x^{4.5} = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^{4.5} \tag{3.3.10}$$

$$\gamma_x \sigma_x^{3.5} = \sum_i \sum_j x_i x_j \gamma_{ij} \sigma_{ij}^{3.5} \tag{3.3.11}$$

The combining rules to calculate the unlike pair interaction characteristic parameters are,

$$\sigma_{ij} = \xi(\sigma_{ii}\sigma_{jj})^{\frac{1}{2}} \tag{3.3.12}$$

$$\varepsilon_{ij} = \zeta = (\varepsilon_{ii}\varepsilon_{jj})^{\frac{1}{2}} \tag{3.3.13}$$

$$\gamma_{ij} = \tfrac{1}{2}(\gamma_{ii} + \gamma_{jj}) \tag{3.3.14}$$

Provided that the binary interaction parameters (BIPs) are avilable, the density of nonpolar mixtures can be calculated accurately using equation (3.3.1) for all fluid phases. The disadvantages of the BWRS equation and the conformal solution model are the facts that the BIPs are not available for

for some mixture systems and polar fluid properties cannot be predicted by this equation of state. Research is being done at the University of Oklahoma to develop an equation of state to include polar and possibly associated fluids. But until that task is done, other equations of state must be used to obtain the density. They physical properties used in BWRS equation are summarized in Table 3.3.2. The BIPs for the semi-empirical exponent mixing rules were recently published for many binary mixture systems by Starling et al (114); some of the BIP's are listed in Table 3.3.3 for both the modified van der Waals and the semiempirical mixing rules respectively.

The density can be estimated for the liquid state using the Hankinson-Thomson correlation (44) which is highly accurate in the saturated liquid region. The Hankinson-Thomson (HT) correlation for the saturated molar volume, V_s, is

$$V_s/V^* = V_R^{(0)} \left(1-\omega_{SRK} V_R^{(\delta)}\right) \tag{3.3.15}$$

where

$$V_R^{(0)} = 1 + a(1-T_R)^{\frac{1}{3}} + b(1-T_R)^{\frac{2}{3}} + C(1-T_R) + d(1-T_R)^{\frac{4}{3}},$$

$$0.25 < T_R < 0.95 \tag{3.3.16}$$

$$V_R^{(\delta)} = (e + fT_R + gT_R^2 + hT_R^3)/(T_R - 1.00001),$$

$$0.25 < T_R < 1.00 \tag{3.3.17}$$

Table 3.3.2 Physical Properties of Pure Fluids For Use With The BWRS Equation (3.3.1)

Fluid	Critical Temp ^{o}F	Critical Density $lb/mole/ft^3$	Molecular Weight	Orientation Parameter γ
Methane	-116.43	0.6274	16.042	0.01289
Ethane	90.03	0.4218	30.068	0.09623
Propane	206.13	0.3121	44.094	0.1538
i-Butane	274.96	0.2373	58.12	0.1812
n-Butane	305.67	0.2448	58.12	0.1991
i-Pentane	369.0	0.2027	72.146	0.2262
n-Pentane	385.42	0.2007	72.146	0.2530
n-Hexane	453.45	0.1696	86.172	0.3054
n-Heptane	512.85	0.1465	100.198	0.3499
n-Octane	563.79	0.1284	114.224	0.4004
n-Nonane	610.5	0.1150	128.24	0.4463
n-Decane	651.9	0.1037	142.276	0.4880
Ethylene	49.82	0.5035	28.05	0.1007
Nitrogen	-232.6	0.6929	28.016	0.0263
Carbon Dioxide	87.8	0.6641	44.01	0.2093
Hydrogen	-400.36	0.9733	2.016	0.0

Table 3.3.3 Binary Interaction Parameter For Use In The BWRS Equation 3.3.1 For The Van Der Waals One Fluid (MvdW) And The Semiempirical (SEE) Mixing Rules

	MvdW		SEE	
Mixture	ξ	ζ	ξ	ζ
CH_4-C_2H_6	0.999079	0.996810	0.999925	0.979586
CH_4-C_3H_8	1.02116	0.974404	1.01188	0.936840
CH_4-C_4H_{10}	1.03946	0.958079	1.02559	0.899345
C_2H_6-C_3H_8	1.0	1.0	1.0	1.0
CH_4-C_2H_4	1.01959	1.01923	--	--
CH_4-$nC_{10}H_{22}$	1.11940	0.978290	1.08519	0.790355
CH_4-N_2	1.02347	0.955616	1.03399	0.96381
C_3H_8-nC_4H_{10}	0.991834	1.00073	--	--
CH_4-iC_4H_{10}	1.05117	0.968823	--	--
CH_4-nC_6H_{14}	1.07738	0.920368	1.05049	0.832570
CH_4-CO_2	0.997963	0.974942	0.98933	0.99122
CH_4-nC_8H_{18}	1.094	0.933	1.05112	0.75148
CH_4-nC_9H_{20}	1.09674	0.937876	1.07753	0.799090
CO_2-N_2	0.985340	1.08098	1.00715	1.08921
nC_4H_{10}-iC_4H_{10}	1.0	1.0	1.0	1.0
H_2-N_2	--	--	1.02116	108378
H_2-CH_4	--	--	1.12777	1.43874
H_2-CO_2	--	--	0.98438	1.39935

$V_R^{(o)}$ represents the isotropic contribution and $V_R^{(\delta)}$ represents the anisotropic contributions. V^* is called the characteristic volume and is very close to the critical volume (within 1.64%) and was determined individually for each compound from experimental density data. ω_{SRK} is the acentric factor determined from the Soave equation of state by regression on experimental density data. T_R is the reduced temperature, T/T_c. Values of V^* and W_{SRK} were reported by Hankinson and Thomson (44) for 200 compounds. The constants in equations (3.3.16) and (3.3.17) are presented in Table 3.3.4.

To apply the HT equation for mixtures, the following mixing rules are used,

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j V^*_{ij} T_{c_{ij}}}{V^*_m} \tag{3.3.18}$$

$$V^*_m = \tfrac{1}{4}[\sum_i x_i V^*_i + 3(\sum_i x_i V_i^{*\frac{2}{3}})\ (\sum_i x_i V_i^{*\frac{1}{3}})] \tag{3.3.19}$$

$$V^*_{ij}\ T_{c_{ij}} = (V^*_i \cdot T_{c_i} \cdot V^*_j\ T_{c_j})^{\frac{1}{2}} \tag{3.3.20}$$

$$W_m = \sum_i x_i \omega_{SRK_i} \tag{3.3.21}$$

The HT equation is superior to other generalized liquid density correlations, particularly in the mixture case. The only disadvantage of this correlation in the present work is that it cannot be applied for the gas phase.

Table 3.3.4 Parameters For Use In The Hankinson-Thomson Equation

a = -1.52816
b = 1.43907
c = -0.81446
d = 0.190454
e = -0.296123
f = 0.386914
g = -0.0427258
h = -0.0480645

3.4 The Viscosity Correlation

A generalized multiparameter corresponding states correlation for viscosity recently has been developed by Chung (19). The correlation is capable of predicting the viscosity of a wide range of fluids such as monatomic fluids, nonpolar and polar polyatomic fluids and fluids with association effects. The capability of the correlation also extends to all fluid states, including the dilute gaseous state, the dense gas state and the liquid state. The form of the correlation is

$$\eta^* = \eta_0^*\left[\frac{1}{GN(y)} + A(6)\cdot Y\right] + A(7)\cdot Y^2 \cdot GN(y)\cdot Exp[B(T^*)] \qquad (3.4.1)$$

where η^* is the reduced viscosity at the fluid condition defined as

$$\eta^* = \frac{\sigma^2\eta}{26.693\sqrt{M(\varepsilon/k)}}$$

where η is the absolute viscosity in micropoise, M is the molecular weight and σ and ε are the characteristic energy parameters and η_0^* is the reduced viscosity in the dilute gas state at the same temperature.

$$Y = (\pi/6)\cdot\rho\cdot\sigma^3 \qquad (3.4.2)$$

$$G = (1-0.5Y)/(1-Y)^3 \qquad (3.4.3)$$

$$GN(Y) = \frac{\{A(1)(1-Exp[-A(4)\cdot Y])/y + A(2)\cdot G\cdot Exp[A(5)\cdot Y]+A(3)\cdot G\}}{[A(1)\cdot A(4) + A(2) + A(3)]} \qquad (3.4.4)$$

$$B(T^*) = A(8) + A(9)/T^* + A(10)/T^{*2} \qquad (3.4.5)$$

The coefficients A(1) through A(10) of equations (3.4.1) through (3.4.5) are given by the relation,

$$A(i) = A_0(i) + \omega \cdot A_1(i) + \mu^{*4} \cdot A_2(i) + \kappa \cdot A_3(i) \qquad (3.4.6)$$

where ω is the Pitzer acentric factor, μ^* is the reduced dipole moment,

$$\mu^* = 100 \cdot \mu/[1.380535(\varepsilon/k)\sigma^3]^{1/2} \qquad (3.4.7)$$

in which μ is the dipole moment in debyes and κ is a parameter which accounts for hydrogen bonding and is referred to as the association parameter. The association parameter κ is unique for each compound and is determined by regression using experimental transport data. For the alcohols, κ was generalized using the relation

$$\kappa = 0.0682 + 0.276659 \cdot \left(\frac{17 \text{ X no. of OH-groups}}{\text{Molecular Weight}}\right) \qquad (3.4.8)$$

Values of $A_0(i)$, $A_1(i)$, $A_2(i)$ and $A_3(i)$ for i =],2,....10 are summarized in Table 3.4.1.

The reduced dilute gas viscosity η_o^* is calculated using the following equation,

$$\eta_o^* = \eta_{CE}^* [1-0.2756 \cdot \omega + 0.0590352 \cdot \mu^{*4} + \kappa] \qquad (3.4.9)$$

where η_{CE}^* is the reduced dilute gas viscosity calculated using the Chapman-Enskog equation,

$$\eta_{CE}^* = T^{*1/2}/\Omega(2,2)^* \qquad (3.4.10)$$

Table 3.4.1 Parameters For Use In The Viscosity Equation

i	$A_0(i)$	$A_1(i)$	$A_2(i)$	$A_3(i)$
1	6.324020	50.411900	-51.680100	1189.020000
2	0.121020×10^{-2}	-0.115361×10^{-2}	-0.625710×10^{-2}	0.372832×10^{-1}
3	5.283460	254.209000	-168.481000	3398.270000
4	6.622630	38.095700	-8.464140	31.417800
5	19.745400	7.630340	-14.354400	31.526700
6	-1.899920	-12.536700	4.985290	-18.150700
7	24.274500	3.449450	-11.291300	69.346600
8	0.797163	1.117640	0.123483×10^{-1}	-4.116610
9	-0.238165	0.676954×10^{-1}	-0.816297	4.025280
10	0.686295×10^{-1}	0.347928	0.592561	-0.726633

where $\Omega(2,2)^*$ is the collision integral determined from the Lennard-Jones (12-6) potential. Neufeld (91) correlated the collision integral $\Omega(2,2)^*$ as

$$\Omega(2,2)^* = \frac{1.16145}{T^{*a}} + 0.52487 \exp(-0.7732T^*) + 2.16178 \exp(-2.43787T^*) - 6.435 \times 10^{-4} T^{*a} \sin(18.0323T^{*b}) - 7.27371 \qquad (3.4.11)$$

where a - 0.14874, b= 0.7683 and T^* is the reduced temperature, $T^* = kT/\varepsilon$. Equation (3.4.11) was used in the determination of η^*_{CE}.

Since the kinetic contribution is dominant in the gas phase and the potential contribution is the main contributor in the liquid phase, the reduced viscosity η^* will be divided into reduced kinetic viscosity η_k and reduced potential viscosity η^*_p, thus,

$$\eta^*_x = \eta^*_{xk} + \eta^*_{xp} \qquad (3.4.12)$$

these contributions are represented in equation (3.4.1) by the following relations

$$\eta^*_{xk} = \eta^*_o \left[\frac{1}{GN(Y)} + A(6) \cdot Y\right] \qquad (3.4.13)$$

and

$$\eta^*_{xp} = A(7) \cdot Y^2 \cdot GN(Y) \text{ Exp } [B(T^*)] \qquad (3.4.14)$$

The mixture viscosity η_x in micropoise is expressed as a function of the reduced viscosity η^*_x, molecular weight M, and the characteristic parameters ε and σ by the relation,

$$\eta_x = 26.693 \frac{\sqrt{\varepsilon_x/k}}{\sigma_x^2} [M_{xk}^{\frac{1}{2}} \eta^*_{xk} + M_{xp}^{\frac{1}{2}} \eta^*_{xp}] \qquad (3.4.15)$$

where $M_{xk} = 2m^*_{xk}N$, $M_{xp} = 2m^*_{xp}N$ and N is Avogadro's number. The characteristic parameters ε and σ are evaluated from equations (3.3.4) and (3.3.5). The physical properties required are summarized in Table 3.4.2. Binary interaction parameters from thermodynamics for both the modified van der Waals one fluid mixing rules and the semi-empirical exponent mixing rules are given in Table 3.3.3 and those values from transport properties are listed in Table 3.4.3.

3.5 The Thermal Conductivity Correlation

Following the same procedure as for viscosity, a generalized multiparameter corresponding states correlation for thermal conductivity also was developed by Chung (19). The correlation has the same capability and range of prediction as the viscosity correlation of equation (3.4.1). The form of the correlation is

Table 3.4.2 Physical Properties of Pure Fluids For Use With The Transport Property Correlations

Fluid	Critical Temp. ^{o}F	Critical Density lb-mole/ft^3	Molecular Weight	Acentric Factor	Dipole Moment Debyes	Association Parameter	$\frac{1}{\beta} = \frac{\rho D}{\eta}$
Neon	-379.75	1.4971	20.183	0.0	0.0	0.0	--
Argon	-188.32	0.8329	39.948	0.0	0.0	0.0	--
Krypton	- 82.75	0.6846	83.800	0.0	0.0	0.0	--
Xenon	61.84	0.5278	131.000	0.0	0.0	0.0	--
Methane	-116.43	0.6274	16.042	0.008	0.0	0.0	--
Ethane	90.03	0.4218	30.068	0.098	0.0	0.0	--
Propane	206.13	0.3121	44.094	0.152	0.0	0.0	--
i-Butane	274.96	0.2373	58.120	0.176	0.0	0.0	--
n-Butane	305.67	0.2448	58.120	0.193	0.0	0.0	--
n-Hexane	453.65	0.1687	86.172	0.296	0.0	0.0	--
n-Heptane	512.85	0.1465	100.198	0.351	0.0	0.0	--
i-Heptane	475.79	0.1495	100.198	0.351	0.0	0.0	--
n-Octane	563.79	0.1284	114.232	0.398	0.0	0.0	--
n-Noname	610.61	0.1139	128.259	0.444	0.0	0.0	--
n-Decane	651.61	0.1039	142.276	0.490	0.0	0.0	--
n-Dodecane	752.27	0.1037	170.340	0.562	0.0	0.0	--
n-Tetradecane	789.53	0.0755	198.394	0.679	0.0	0.0	--
n-Hexadecane	830.93	0.0662	226.448	0.752	0.0	0.0	--
n-Octadecane	881.33	0.0589	254.502	0.790	0.0	0.0	--
Ethylene	49.82	0.5035	28.050	0.085	0.0	0.0	--
Carbon Dioxide	87.80	0.6641	44.010	0.225	0.0	0.0	--
Nitrogen	-232.60	0.6929	28.016	0.040	0.0	0.0	--
Oxygen	-181.30	0.8505	31.999	0.021	0.0	0.0	--
Hydrogen	-400.36	0.9605	2.016	0.0	0.0	0.0	1.32

Table 3.4.2 (Continued)

Fluid	Critical Temp. ^{o}F	Critical Density lb-mole/ft^3	Molecular Weight	Acentric Factor	Dipole Moment Debyes	Association Parameter	$\frac{1}{\beta} \approx \frac{\rho D}{\eta}$
Carbon Tetrachloride	541.85	0.2262	153.825	0.689	0.0	0.0	1.32
Tetrafluoromethane	- 49.99	0.4459	88.005	0.191	0.0	0.0	--
Benzene	552.09	0.2420	78.115	0.212	0.0	0.0	1.32
P-Xylene	649.43	0.1650	106.169	0.324	0.0	0.0	--
O-Xylene	674.69	0.1692	106.169	0.275	0.0	0.0	--
Chlorene	290.93	0.5305	70.906	0.073	0.0	0.0	--
Toluene	699.44	0.1965	92.134	0.196	0.43	0.0	1.58
Cyclohexane	536.53	0.2027	84.163	0.213	0.61	0.0	--
Naphthalene	887.45	0.1511	128.173	0.302	0.0	0.0	--
Cyclopentane	461.21	0.2401	70.135	0.192	0.0	0.0	--
Dichloromethane	458.33	0.3235	84.933	0.193	1.54	0.0	1.32
Methylchloride	505.85	0.2612	119.378	0.216	1.10	0.0	1.32
Ammonia	270.41	0.8614	17.031	0.250	1.47	0.0	1.08
Sulfur Dioxide	315.77	0.5117	64.063	0.251	1.60	0.0	1.16
Nitrous Oxide	97.61	0.6410	44.013	0.160	0.20	0.0	1.33
Chlorotrifluoromethane	83.93	0.3468	104.459	0.180	0.50	0.50	--
Chlorodifluoromethane	204.89	0.3784	86.469	0.215	1.405	0.0	--
Benzonitrile	799.25	0.1720	103.124	0.172	3.50	0.0	--
Chloroform	505.85	0.2612	119.378	0.216	1.10	0.0	1.32
Diethyle Ether	380.39	0.2230	74.123	0.281	1.30	0.0	1.32
Dimethyl Ether	260.33	0.3507	46.069	0.192	1.30	0.0	1.48
Water	705.47	1.1148	18.015	0.344	1.80	0.0759	0.78
Tetrahydrofuran	512.69	0.2787	72.017	0.221	1.70	0.1627	--

Table 3.4.2 (Continued)

Fluid	Critical Temp. ^{o}F	Critical Density lb-mole/ft^3	Molecular Weight	Acentric Factor	Dipole Moment Debyes	Association Parameter	$\frac{1}{\beta} = \frac{\rho}{\eta}$
Methanol	463.01	0.5291	32.042	0.559	1.70	0.1627	--
Ethanol	469.49	0.3738	46.069	0.635	1.73	0.1748	1.31
n-Propanol	506.39	0.2857	60.096	0.624	1.70	0.1435	1.43
s-Propanol	455.27	0.2838	60.096	0.6637	1.70	0.1435	1.43
n-Butanol	553.55	0.2278	74.123	0.590	1.80	0.1317	1.48
i-Butanol	526.18	0.2287	74.123	0.588	1.70	0.1317	1.48
s-Butanol	505.13	0.2329	74.123	0.570	1.70	0.1317	1.48
n-Pentanol	595.13	0.1915	88.150	0.580	1.70	0.1216	1.40
n-Hexanol	638.33	0.1639	102.177	0.560	1.80	0.1142	1.50
n-Heptanol	679.73	0.1435	116.204	0.560	1.70	0.1087	1.46
Phenol	789.89	0.2726	94.113	0.440	1.60	0.1020	1.54
Aniline	798.53	0.2312	93.129	0.382	1.60	0.0330	1.32
Acetric Acid	610.25	0.3651	60.052	0.454	1.55	0.0915	--
Acetone	455.00	0.2987	58.080	0.309	2.69	0.1997	1.42
Methylethyl Ketone	504.41	0.2338	72.107	0.329	3.30	0.1849	1.32
Methylpropyl Ketone	555.53	0.2074	86.134	0.348	2.50	0.2016	--
4-Methyl-2-Pentone	568.13	0.1683	100.161	0.400	2.80	0.1443	--

Table 3.4.3 Values of The Binary Interaction Parmater ξ^*_{ij} Determined From Regression On Experimental Transport Data For The Modified Van Der Waals (MvdW) And The Semiempirical Exponent (SEE) Mixing Rules

Mixture	MvdW		SEE	
	Viscosity	Thermal Conductivity	Viscosity	Thermal Conductivity
C_2H_6-$nC_{10}H_2$	1.14673	--	1.12747	--
CH_4-CF_4	0.854696	--	0.744297	--
$nC_{16}H_{34}$-nC_6H_{14}	1.03393	--	1.02236	--
$nC_{14}H_{30}$-nC_6H_{14}	1.02032	--	1.01318	--
nC_7H_{16}-$nC_{12}H_{26}$	0.975791	--	0.969883	--
nC_7H_{16}-$nC_{14}H_{30}$	1.01041	--	1.01041	--
nC_7H_{16}-$nC_{16}H_{30}$	1.02245	--	1.01465	--
nC_7H_{16}-$nC_{18}H_{38}$	1.02917	--	1.01845	--
iC_7H_{16}-$nC_{12}H_{26}$	0.987973	--	0.982677	--
iC_7H_{16}-$nC_{16}H_{34}$	1.03368	--	1.02582	--
Toluene-nC_8H_{18}	0.984181	--	0.981727	--
Benzene-$nC_{16}H_{34}$	1.06883	--	1.04389	--
Benzene-$nC_{12}H_{26}$	1.00378	--	0.982439	--
Benzene-$nC_{14}H_{30}$	1.04934	--	1.02934	--
Benzene-$nC_{18}H_{38}$	1.07764	--	1.04895	--
Methanol-Water	1.07337	0.840228	1.06693	0.847111
Ethanol-Water	1.16122	0.798917	1.14805	0.796332
n-Propanol-Water	1.0	0.781813	1.0	0.769529
Acetone-Water	1.0	0.93384	1.0	0.930809

Table 3.4.3 (Continued)

Mixture	MvdW		SEE	
	Viscosity	Thermal Conductivity	Viscosity	Thermal Conductivity
Tetrahydrofuran-Water	1.16032	--	1.13343	--
Acetone-Acetic Acid	1.03546	--	1.03540	--
Chloroform-Acetic Acid	1.01307	--	1.01235	--
4-Methyl-2-Pentone-Acetic Acid	1.02481	--	1.01635	--
Chloroform-Methyl Ethyl Ketone	--	1.11499	--	1.11573
Toluene-Methyl Ethyl Ketone	--	1.11400	--	1.10780
Acetone-Methyl Ethyl Ketone	--	0.983601	--	0.983301
CCl_4-i-Butanol	--	0.929373	--	0.926398
CCl_4-n-Butanol	--	0.938974	--	0.938539
CCl_4-S-Propanol	--	0.941557	--	0.936528
CCl_4-S-Butanol	--	0.943512	--	0.940179
CCl_4-n-Pentanol	--	0.948103	--	0.947340
Cyclohexane-n-Propanol	--	0.953460	--	0.950146
n-Butanol-Methylisbutyl Ketone	1.01307	--	1.01235	--

*$\zeta = 1.0$

$$\lambda^* = \lambda_o^* \left[\frac{1}{GM(Y)} + A(6) \cdot Y\right] + A(7) \cdot Y^2 \cdot T^{*\frac{1}{2}} \cdot GM(Y) \qquad (3.5.1)$$

where λ^* is the reduced thermal conductivity at the fluid condition defined as

$$\lambda^* = \frac{\sigma \lambda}{19{,}891\left(\frac{\varepsilon/k}{M}\right)^{\frac{1}{2}}}$$

where λ is the thermal conductivity in cal/cm-sec-^{o}R X 10^5, M is the molecular weight, and σ and ε are the characteristic energy parameters and λ_o^* is the reduced thermal conductivity in the dilute case,

$$Y = (\pi/6) \cdot \rho \cdot \sigma^3 \qquad (3.5.2)$$

$$G = (1-0.5Y)/(1-Y)^3 \qquad (3.5.3)$$

$$GM(Y) = \frac{\{A(1)(1-Exp[-A(4)\cdot Y])/Y+A(2)\cdot G\cdot Exp[A(5)\cdot Y]+A(3)\cdot G\}}{[A(1)\cdot A(4)+A(2)+A(3)]} \qquad (3.5.4)$$

The coefficients A(1) through A(7) are generalized using the relation

$$A(i) = A_0(i) + \omega \cdot A_1(i) + \mu^{*4} \cdot A_2(i) + \kappa \cdot A_3(i) \qquad (3.5.5)$$

where ω is the Pitzer acentric factor, μ^* is the reduced dipole moment, and κ is the association parameter. The coefficients $A_0(i)$, $A_1(i)$, $A_2(i)$ and $A_3(i)$ for i = 1,2,...7 are given in Table 3.5.1.

Table 3.5.1 Parameters For Use In Thermal Conductivity Equation

i	$A_0(i)$	$A_1(i)$	$A_2(i)$	$A_3(i)$
1	2.416570	0.748240	0.918581	121.721000
2	-0.509237	-1.509360	-49.991200	69.983400
3	6.610690	5.620730	64.759900	27.038900
4	14.542500	-8.913870	-5.637940	74.343500
5	0.792741	0.820189	-0.693692	6.317340
6	-5.863400	12.800500	9.589260	65.52900
7	81.171000	114.158000	-60.841000	446.775000

The dilute gas reduced thermal conductivity λ_o^* is calculated from the following equation,

$$\lambda_o^* = \eta_o^* \left[\frac{1+C_{int}^*(0.215-1.061 \cdot \beta/Z_{coll} + 0.28288 \frac{C_{int}^*}{Z_{coll}}}{\beta + 0.6366/Z_{coll} + 1.061 \frac{C_{int}^*}{Z_{coll}}}\right] \quad (3.5.6)$$

where η_o^* is the reduced dilute gas viscosity given by equation (3.4.9), $C_{int}^* = C_{int}/R$ which is the reduced internal heat capacity at constant volume,

$$C_{int}^* = C_v^* - C_{tr}^* \quad (3.5.7)$$

and

$$C_{tr}^* = C_{tr}/R = \frac{2}{3} \quad (3.5.8)$$

C_{tr} is the ideal gas translational heat capacity at constant volume which in this case is forced to be $\frac{2}{3}$ R in order to satisfy the monatomic ideal gas requirement. The ideal gas heat capacity at constant volume is calculated from the relation,

$$C_v = C_p - 1 \quad (3.5.9)$$

where C_p is the heat capacity at constant pressure. C_p was obtained from the relation given by Reid et al (98),

$$C_p = a + bT + cT^2 + dT^3 \qquad (3.5.10)$$

where the constants a, b, c and d are determined individually for each component and are listed in reference (98). Other correlations could of course be used for C_p.

The term Z_{coll} in equation (3.5.1) represents the number of collisions required to interchange a quantum of internal energy with translational energy. Z_{coll} is correlated as a function of the reduced temperature T^* as,

$$Z_{coll} = 2.0 + 6.6T^{*2} \qquad (3.5.11)$$

The parameter β is defined as,

$$\beta = \eta/\rho D \qquad (3.5.12)$$

where η is the viscosity, D is the self-diffusion coefficient and ρ is the density. β is around 1/1.32 for many fluids but this assumption is not always true. The value of β is determined individually from experimental data in the dilute gas state where the thermal conductivity is very sensitive to β. In the liquid phase the value of 1/1.32 is adequate for accuate prediction. For hydrocarbons, β can be generalized as a function of the acentric factor ω,

$$\beta = 0.786231 - 0.710907 \cdot \omega + 1.31683 \cdot \omega^2 \qquad (3.5.13)$$

As was done in the viscosity case, the thermal conductivity is also divided into a kinetic contribution λ^*_k and a potential contribution λ^*_p, thus

$$\lambda^*_x = \lambda^*_{xk} + \lambda^*_{xp} \tag{3.5.14}$$

where x represents the hypothetical reference fluid in the conformal solution model. Both contributions are represented in equation (3.5.1) by,

$$\lambda^*_{xk} = {}^*_o [\frac{1}{GM(Y)} + A(6) \cdot Y] \tag{3.5.15}$$

and

$$\lambda^*_{xp} = A(7) \cdot Y^2 \cdot T^{*\frac{1}{2}} \cdot GM(Y) \tag{3.5.16}$$

The ideal gas heat capacity at constant volume C^*_{vx} is calculated as,

$$C^*_{vx} = \sum_i x_i C^*_{vi} \tag{3.5.17}$$

and the parameter β_x can be calculated using equation (3.5.13) for hydrocarbon mixtures; otherwise, β_x can be obtained from

$$\beta_x = \sum_i x_i \beta_i \tag{3.5.18}$$

In the case of liquid mixture, a value of $\beta_x = 1/1.32$ will yield good results.

The thermal conductivity, λ_x in $\frac{\text{cal}}{\text{cm-sec-}^oF} \times 10^5$, is expressed as function of the reduced thermal conductivity λ^*, the molecular weight and the characteristic parameters ε and σ by the relation

$$\lambda_x = 19.891 \frac{\sqrt{\varepsilon_x/\kappa}}{\sigma_x^2} \left[\frac{\lambda^*_{xk}}{M_{xk}^{\frac{1}{2}}} + \frac{\lambda^*_{xp}}{M_{xp}^{\frac{1}{2}}} \right] \qquad (3.5.19)$$

where $M_{xk} = 2\, m^*_{xk} N$, $M_{xp} = 2\, m^*_{xp} N$ and N is Avogadro's number. The characteristic parameters ε and σ are calculated using equations (3.3.4) and (3.3.5).

3.6 Empirical Model For Nonpolar Mixture Viscosity

Even though, the conformal solution theory model is powerful and easy to use, it has some disadvantages. The accuracy of prediction is not acceptable when the mixture constituents are highly dissimilar in size such as methane + n-Decane, therefore, to improve the accuracy, binary interaction parameters are required which are not easily available or unknown for many mixture systems. For these reasons, this empirical model is presented to avoid those difficulties.

The idea of this model is to calculate the coefficient of viscosity as functions of the coefficients of the pure individual constituents of the mixture. Then, these coefficients are mixed as functions of the mixture composition where no binary interaction parameters are needed.

The reduced kinetic viscosity η_k^* and potential viscosity, η_p^* given by equations (3.4.13) and (3.4.14) are unreduced according to equation (3.4.15) to give the following relations

$$\eta_k = Y \left[\frac{D_1 \eta_o}{A`(1)\,(1-\exp(-A`(4)Y`)+C_4\,(A(2)\,\mathrm{Exp}(A`(5)Y`)+A(3)} + \eta_o\, A`(6)\right] \tag{3.6.1}$$

and

$$\eta_p = \frac{C_2}{D_1} A`(7)A`(1)\mathrm{Exp}[B(T^*)]\,(1-\mathrm{Exp}(A`(4)Y`) + \frac{C_3}{D_1} A`(7)A(2)\mathrm{Exp}[B(T^*)]\mathrm{Exp}(A`(5)Y`) + \frac{C_3}{D_1} A`(7)A(3)\mathrm{Exp}[B(T^*)] \tag{3.6.2}$$

and

$$\eta = \eta_k + \eta_p \tag{3.6.3}$$

where η is the viscosity in micropoise. The coefficients of equations (3.6.1) and (3.6.2) are defined as

$$Y` = \frac{\pi}{6}\rho \tag{3.6.4}$$

$$D_1 = A(1)A(4) + A(2) + A(3) \tag{3.6.5}$$

$$A`(1) = A(1)/\sigma^3 \tag{3.6.6}$$

$$A`(4) = A(4)\sigma^3 \tag{3.6.7}$$

$$A`(5) = A(5)\sigma^3 \tag{3.6.8}$$

$$A`(6) = A(6)\sigma^3 \tag{3.6.9}$$

$$A`(7) = A(7)\sqrt{M(\varepsilon/k)} \cdot \sigma^4 \tag{3.6.10}$$

$$\eta_o = \eta_o^* \left[\frac{26.693\ M(\varepsilon/k)}{\sigma^2}\right] \tag{3.6.11}$$

$$C1 = 26.693\ Y`^2 \tag{3.6.12}$$

$$C2 = C1/Y` \tag{3.6.13}$$

$$C3 = C1 \cdot G \tag{3.6.14}$$

$$C4 = G \cdot Y` \tag{3.6.15}$$

Let,

$$BY = A`(7)A`(1)\mathrm{Exp}[B(T^*)] \tag{3.6.16}$$

$$BZ = A`(7)A(2)\mathrm{Exp}[B(T^*)] \tag{3.6.17}$$

$$BX = A\ (7)A(3)\mathrm{Exp}[B(T^*)]/D1 \tag{3.6.18}$$

$$F1 = \eta_o\ A`(6) \tag{3.6.19}$$

$$E1 = \eta_o D1 \tag{3.6.20}$$

Inserting equations (3.6.16) through (3.6.20) into equations (3.6.1) and (3.6.2), the following forms are obtained,

$$\eta_k = Y`\left[\frac{E1 \cdot D1}{A`(1)\,(1-\mathrm{Exp}(-A`(4)Y`)+C_4(A(2)\mathrm{Exp}(A`(5)Y`+A(3)} + F1)\right] \tag{3.6.21}$$

$$\eta_p = \frac{C2 \cdot BY}{D1}\,(1-\mathrm{Exp}(A\grave{}(4)Y\grave{}) + \frac{C3 \cdot BZ}{D1}\,\mathrm{Exp}(A\grave{}(5)Y\grave{}) + C3 \cdot BX \qquad (3.6.21)$$

Mixing Rules:

$$\sigma_m^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \qquad (3.6.22)$$

where σ_m is the characteristic distance parameter for the mixutre to be applied for the calculation of the term G of equation (3.4.3) in order to calculate Y`.

$$Dl_m = \sum_i \sum_j x_i x_j Dl_{ij} \qquad (3.6.23)$$

$$BY_m = \sum_i \sum_j x_i x_j BY_{ij} \qquad (3.6.24)$$

$$BZ_m = \sum_i \sum_j x_i x_j BZ_{ij} \qquad (3.6.25)$$

$$BX_m = \sum_i \sum_j x_i x_j BX_{ij} \qquad (3.6.26)$$

$$A_m\grave{}(4) = \sum_i \sum_j x_i x_j A_{ij}\grave{}(4) \qquad (3.6.27)$$

$$A_m\grave{}(5) = \sum_i \sum_j x_i x_j A_{ij}\grave{}(5) \qquad (3.6.28)$$

$$A_m\grave{}(1) = \sum_i \sum_j x_i x_j A_{ij}\grave{}(1) \qquad (3.6.29)$$

$$A_m(2) = \sum_i \sum_j x_i x_j A_{ij}(2) \qquad (3.6.30)$$

$$A_m(3) = \sum_i \sum_j x_i x_j A_{ij}(3) \tag{3.6.31}$$

$$\eta_{o,m} = \sum_i \sum_j x_i x_j \eta_{o,ij} \tag{3.6.32}$$

$$El_m = \eta_{o,m}/Dlm \tag{3.6.33}$$

$$Fl_m = \sum_i \sum_j x_i x_j Fl_{ij} \tag{3.6.34}$$

The terms Dl_{ij}, BY_{ij}, BX_{ij}, $A_{ij}(4)$, $A_{ij}(1)$, $A_{ij}(2)$, $A_{ij}(3)$ and $\eta_{o,ij}$ are obtained from

$$H_{ij} = (H_{ii} \cdot H_{jj})^{\frac{1}{2}} \tag{3.6.35}$$

where H represents each of the above terms. The terms BZ_{ij}, $A_{ij}(5)$ and Fl_{ij} are obtained from

$$L_{ij} = \frac{(L_{ii} + L_{jj})}{2} \tag{3.6.36}$$

where L represents each of the above terms.

CHAPTER IV

VISCOSITY

RESULTS AND DISCUSSION

The conformal solution theory approach discussed in Chapter III was applied to predict the viscosity of binary mixtures in all fluid ranges. The generalized viscosity equation (3.4.1) was applied in the prediction of binary mixtures and the results were compared to the experimental data. The mixtures covered a wide variety of components such as monatomic, polar and nonpolar polyatomic and associating fluids. The mixture systems ranged from dilute gas mixtures to dense gas mixtures to liquid mixtures. The mixtures and experimental data ranges are presented in Table 4.1.

The mixing rules for the characterization parameters, σ_x, ε_x, ω_x, μ_x, κ_x and m_x^* were presented in Table 3.2.1 of Chapter III. As was shown in this table, two sets of mixing rules were presented as set A and set B. These mixing rules will be referred to in this discussion as method A for the modified van der Waals one fluid mixing rules and method B for the semiempirical exponent mixing rules.

Table 4.1: Experimental Viscosity Data Ranges and References

Mixture	No. of Points	Temp. Range, ^{o}R	Press. Range, Psia	Composition	Reference
Ar-Kr	65	540-2,700	14.696	1.00-0.00	Kestin (64)
Ar-Ne	78	527- 545	14.696-752	1.00-0.00	Kestin (62)
CH_4-C_2H_6	20	527- 942	14.696	1.00-0.00	Trautz (122)
C_2H_6-C_3H_8	20	527- 942	14.696	1.00-0.00	Trautz (122)
CH_4-nC_4H_{10}	41	527- 545	15.43-96.70	0.8432-0.00	Kestin (63)
nC_4H_{10}-iC_4H_{10}	29	537- 672	14.696	1.00-0.00	Abe (1)
CH_4-CO_2	56	527- 545	15.43-373	1.00-0.00	Kestin (63)
CH_4-C_3H_8	468	559- 919	14.696-10,000	0.30-0.70	Lee (67)
CH_4-C_3H_8	140	222- 560	500-5,000	0.221-0.753	Huang (53)
CH_4-nC_4H_{10}	118	559- 799	200-8,000	0.25-0.90	Lee (67)
CH_4-$nC_{10}H_{22}$	71	559- 739	1,500-7,000	0.30-0.70	Lee (68)
CH_4-$nC_{10}H_{22}$	29	460- 589	100-1,200	0.033-0.404	Bagzis (2)
CH_4-CO_2	132	581- 853	490-10,000	0.243-0.755	DeWitt (22)
CH_4-CF_4	192	581- 853	480-6,027	0.00-0.75	DeWitt (23)
CH_4-nC_6H_{14}	4	460	100-1,200	0.055-0.475	Bagzis (2)
CH_4-nC_9H_{20}	32	429- 537	150-1,200	0.052-0.326	Bennett (9)
C_2H_6-$nC_{10}H_{22}$	18	490- 633	50-300	0.051-0.359	Bagzis (2)
H_2-CH_4	219	311- 491	59-7,337	0.00-1.00	Chuang (16)
Naphthalene-Benzene	10	635	14.696	0.00-0.900	Cambell (13a)
$nC_{16}H_{34}$-nC_6H_{14}	20	536.67	14.696	0.0553-0.766	Heric (47)
$nC_{16}H_{34}$-nC_6H_{14}	2	527- 510	14.696	0.50	Dixon (24)
$nC_{14}H_{30}$-nC_6H_{14}	10	536.67	14.696	0.0545-0.7946	Heric (47)

Table 4.1 (Continued)

Mixture	No. of Points	Temp. Range, °R	Press. Range, Psia	Composition	Reference
Benzene-$nC_{16}H_{34}$	9	536- 67	14.696	0.0317-0.7656	Heric (47)
Benzene-$nC_{16}H_{34}$	6	536- 604	14.696	0.50	Trevoy (123)
Benzene-$nC_{12}H_{26}$	3	536- 604	14.696	0.50	Trevoy (123)
Benzene-$nC_{14}H_{30}$	3	536- 604	14.696	0.50	Trevoy (123)
Benzene-$nC_{18}H_{38}$	3	536- 604	14.696	0.50	Trevoy (123)
$nC_{16}H_{34}$-$nC_{14}H_{30}$	11	536.67	14.696	0.0861-0.973	Heric (47)
nC_7H_{16}-$nC_{14}H_{30}$	3	536- 604	14.696	0.50	Trevoy (123)
nC_7H_{16}-$nC_{16}H_{34}$	3	536- 604	14.696	0.50	Trevoy (123)
nC_7H_{16}-$nC_{18}H_{38}$	3	536- 604	14.696	0.50	Trevoy (123)
nC_7H_{16}-$nC_{12}H_{26}$	6	536- 604	14.696	0.50	Trevoy (123)
iC_7H_{16}-$nC_{12}H_{26}$	3	536- 604	14.696	0.50	Trevoy (123)
iC_7H_{16}-$nC_{16}H_{34}$	3	356- 604	14.696	0.50	Trevoy (123)
Benzene-iC_7H_{16}	3	536- 604	14.696	0.50	Trevoy (123)
Benzene-nC_7H_{16}	3	536- 604	14.696	0.50	Trevoy (123)
Benzene-nC_6H_{14}	10	536.67	14.696	0.1795-0.9253	Heric (47)
CCl_4-nC_6H_{14}	8	536.67	14.696	0.1447-0.8872	Heric (47)
CCl_4-Benzene	9	536.67	14.696	0.0927-0.8882	Heric (47)
Toluene-nC_8H_{18}	28	545- 662	14.696	1.00-0.00	Ling (73)
Ar-NH_3	130	527- 545	14.696-360	1.00-0.00	Iwasaki (54)
Ar-NH_3	32	536- 635	14.696	1.00-0.00	Chakraborti (15)
N_2O-NH_3	276	536- 672	14.696-1,750	1.00-0.00	Hongo (48)
CH_4-NH_3	33	536- 635	14.696	1.00-0.00	Chakrabroti (15)
N_2O-NH_3	33	536- 635	14.696	1.00-0.00	Chakrabroti (15)
Ar-SO_2	35	536- 635	14.696	1.00-0.00	Chakrabroti (15)
N_2O-SO_2	34	536- 635	14.696	1.00-0.00	Chakrabroti (15)

Table 4.1 (Continued)

Mixture	No. of Points	Temp. Range, ^{o}R	Press. Range, Psia	Composition	Reference
CO_2-SO_2	37	536- 635	14.696	1.00-0.00	Chakrabroti (15)
CH_4-SO_2	19	536- 635	14.696	1.00-0.00	Chakrabroti (15)
N_2-$CClF_3$	19	536- 582	15.70-74.70	0.156-0.823	Tanaka (117)
N_2-$CHClF_2$	21	536- 582	15.70-74.70	0.286-0.824	Tanaka (117)
Benzene-Benzonitrile	9	545	14.696	1.00-0.00	Reddy (97)
CH_3Cl-SO_2	21	554- 635	14.696	1.00-0.00	Chakrabroti (14)
$(CH_3)_2O$-CH_3Cl	21	554- 635	14.696	1.00-0.00	Chakrabroti (14)
$(CH_3)_2O$-SO_2	22	554- 635	14.696	1.00-0.00	Chakrabroti (14)
Methanol-Water	8	671.67	14.696	1.00-0.00	Silgardo (106)
Ethanol-Water	11	671.67	14.696	1.00-0.00	Silgardo (106)
Methanol-Water	156	509- 626	14.50-9.971	1.00-0.00	Kubota (65)
Methanol-Water	60	536- 581	14.696	1.00-0.00	Mikhail (83)
Ethanol-Water	87	536- 581	14.5-11,385	1.00-0.00	Tanaka (116)
n-Propanol-Water	19	545- 626	14.696	1.00-0.00	Ling (73)
Acetone-Water	93	527- 671	14.696	1.00-0.00	Howard (51)
Acetone-Acetic Acid	11	592- 705	14.696	1.00-0.00	Howard (52)
Toluene-Acetone	44	527- 572	14.696	1.00-0.00	Hafez (43)
4-Methyl-2-Pentone-Acetic Acid	44	527- 572	14.696	1.00-0.00	Hafez (43)
Chloroform-Acetic Acid	18	536.67	14,696	1.00-0.00	Vitagliano (128)
n-Butanol-Methyl Isobutyl Ketone	41	545- 599	14.696	1.00-0.00	Dakshinamurty (20)

Table 4.1 (Continued)

Mixture	No. of Points	Temp. Range, ^{o}R	Press. Range, Psia	Composition	Reference
Tetrahydrofuran-Water	18	536.67	14.696	1.00-0.00	Hayduk (47)
Benzene-Acetone	10	592- 634	14.696	1.00-0.00	Howard (52)
Benzene-Methyl Ethyl Ketone	53	433- 538	14.696	1.00-0.00	Teller (118)
Benzene-Methyl Propyl Ketone	10	545.67	14.696	1.00-0.00	Reddy (97)

The objective of this work was to accurately predict the mixture viscosity with the same parameters needed for prediction of the pure fluid viscosity. This means that the unlike pair interaction parameters σ_{ij} and ε_{ij}, which are obtained from equation (3.2.14) and (3.2.15), have to be calculated without the need for binary viscosity data to determine the binary interaction parameters ξ_{ij} and ζ_{ij} for σ_{ij} and ε_{ij}, respectively. Thus, the first objective was to find out if these parameters ξ_{ij} and ζ_{ij} could be taken as unity in equation (3.2.14) and (3.2.15). If this approach would not work acceptably, then the second objective was to obtain the values of ξ_{ij} and ζ_{ij} from thermodynamics. The reason for using the thermodynamic values is to maintain self-consistancy between transport and thermodynamic properties. However, ξ_{ij} and ζ_{ij} have not been determined for the polar and associated mixtures from thermodynamic data. Therefore, the third objective was to abstract ξ_{ij} and ζ_{ij} from experimental transport data. The above objectives will be referred to in this work as objective I, II and III, respectively.

The need for the binary interaction parameters ξ_{ij} and ζ_{ij} will sometimes cause a problem because of their limited availability, especially when the viscosity of a new mixture is needed. The solution for this problem would

be either to generalize these parameters in terms of some known properties of the constituent pure compnents or to assign a unity value to both of them. The later alternative is more attractive if the accuracy of prediction were found to be within an acceptable range. The question then arises about what is the acceptable value of accuracy? In most engineering practical design applications, 10 to 20% average absolute deviation is acceptable to the designer but this high deviation was not by any means the standard for this work, as will be shown later.

Dilute gas mixtures will be discussed in the following paragraphs. This case was divided into several mixture categories such as nonpolar mixtures, polar mixtures, polar-nonpolar mixtures and mixtures with association effects. The results presented here were obtained with unity binary interaction parameters. Table 4.2 presents a summary of the results for the dilute nonpolar gas mixture systems predicted in this work. The systems include some monatomic mixtures as well as polyatomic mixtures. The viscosities of a total of 309 points were predicted and compared with experimental data points. Unfortunately, experimental data are relatively unavailable in the dilute gas phase for systems with greatly different molecular size constituents such as methane with long chain hydrocarbons. The average absolute deviation for the 309 nonpolar mixture points was 1.63% and 2.43% for

Table 4.2: Summary of Results For The Viscosity of Dilute Nonpolar Gas Mixtures.

Mixtures	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
Ar-Kr	65	2.57	3.57	Kestin (64)
Ar-Ne	78	0.79	2.24	Kestin (62)
CH_4-C_2H_6	20	0.81	0.92	Trautz (122)
C_2H_6-C_3H_8	20	2.25	2.27	Trautz (122)
CH_4-nC_4H_{10}	41	0.78	0.44	Kestin (63)
nC_4H_{10}-iC_4H_{10}	29	0.54	0.54	Abe (1)
CH_4-CO_2	56	2.96	4.71	Kestin (63)
Overall	309	1.63	2.43	

*The binary interaction parameters are taken to be unity ($\xi=\zeta=1.0$)

†Avg. Abs. Dev. % = $[\Sigma|\eta_{exp}-\eta_{cal}|/\eta_{exp}]$ X 100/No. of Points

method A and method B, respectively.

Table 4.3 presents a summary of the results for dilute polar mixtures in which the viscosity of only 64 points were predicted. Experimental data are scarce in the dilute state for this class of mixtures. More experimental data are needed to justify any conclusions for this class of mixture. The average absolute deviation (AAD) is 3.28% for method A and 3.34% for method B.

Table 4.4 presents the results for dilute gas polar-nonpolar mixtures. The viscosity of a toal of 669 points were predicted with an AAD of 4.75% by method A and 4.02% by method B.

Finally, Table 4.5 presents the results for dilute gas mixtures with association effects. Few experimental systems were available for comparison and only the viscosity of 19 points were predicted, with an AAD of 3.29% for method A and 3.45% for method B. It is clear that more systems of this class have to be tested for valid conclusions to be drawn.

In general, the viscosity of dilute gas mixtures is predicted accurately by the conformal solution theory approach. Both sets of mixing rules, the modified van der Waals one fluid mixing rules, (method A) and the semiempirical exponent mixing rules (method B) produce almost the same accuracy for viscosity prediction. The overall average absolute deviation

Table 4.3: Summary of Results For The Viscosity of Dilute Polar Gas Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
CH_3Cl-SO_2	21	2.83	2.83	Chakrabroti (14)
$(CH_3)_2O-CH_3Cl$	21	3.02	3.04	Chakrabroti (14)
$(CH_3)_2O-SO_2$	22	3.95	4.11	Chakrabroti (14)
Overall	64	3.28	3.34	

*Binary interaction parameters are taken to be unity ($\xi=\zeta=1.0$)

†Avg. Abs. Dev. % = $[\Sigma|\eta_{exp}-\eta_{cal}|/\eta_{exp}]$ X 100/No. of Points

Table 4.4: Summary of Results For The Viscosity of Dilute Nonpolar-Polar Gas Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
$Ar-NH_3$	130	8.61	7.22	Iwasaki (54)
$Ar-NH_3$	32	7.31	5.36	Chakraborti (15)
N_2-NH_3	276	3.87	2.90	Hongo (48)
CH_4-NH_3	33	1.83	1.25	Chakraborti (15)
N_2O-NH_3	33	7.12	8.18	Chakraborti (15)
$Ar-SO_2$	35	3.43	2.04	Chakraborti (15)
N_2O-SO_2	34	2.38	2.26	Chakraborti (15)
CO_2-SO_2	37	2.02	1.89	Chakraborti (15)
CH_4-SO_2	19	2.64	6.05	Chakraborti (15)
N_2-CClF_3	19	3.04	1.89	Tanaka (117)
$N_2-CHClF_2$	21	3.63	4.68	Tanaka (117)
Overall	669	4.75	4.02	

*Binary interaction parameters are taken to be unity ($\xi=\zeta=1.0$)

†Avg. Abs. Dev. % = $[\Sigma|\eta_{exp}-\eta_{cal}|/\eta_{exp}]$ X 100/No. of Points

Table 4.5: Summary of Results of The Viscosity of Dilute Gas Mixtures With Association Forces

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
Methanol-Water	8	2.41	2.46	Silgardo (106)
Ethanol-Water	11	3.92	4.16	Silgardo (106)
Overall	19	3.29	3.45	

*Binary interaction parameters are taken to be unity ($\xi=\zeta=1.0$)

†Avg. Abs. Dev. % = $[\Sigma|\eta_{exp}-\eta_{cal})/\eta|_{exp}]$ X 100/No. of Points

for the dilute gas mixtures was 3.73% and 3.51% for method A and method B respectively.

All the dilute gas predictions were obtained by taking unity values for the binary interaction parameters. Thus, the first objective of this work was achieved satisfactorly without the need for values for the binary interaction parameters obtained from data.

Comparisons between experimental and predicted viscosities for some selected dilute gas mixture systems are illustrated graphically in Figures 4.1 through 4.11.

In a manner similar to that used for dilute gas mixtures, the accuracies of viscosity predictions for the dense gas and liquid mixtures will now be discussed.

Table 4.6 presents results for nonpolar dense gas and liquid mixture systems. But in this case, the tabulation of the average absolute deviation is slightly different from those of the dilute gas mixtures. It was found that some of the system's predictions were not accurate when the binary interaction parameter ξ_{ij} and ζ_{ij} were given unity values, especially when the mixture constituents are of largely dissimilar sizes. Therefore, values of the binary interaction parameters were obtained from the thermodynamic literature if they were available and if not, then values were determined by regression on experimental viscosity data. Thus, in Table 4.6 and the succeeding tables, the headings I, II and III

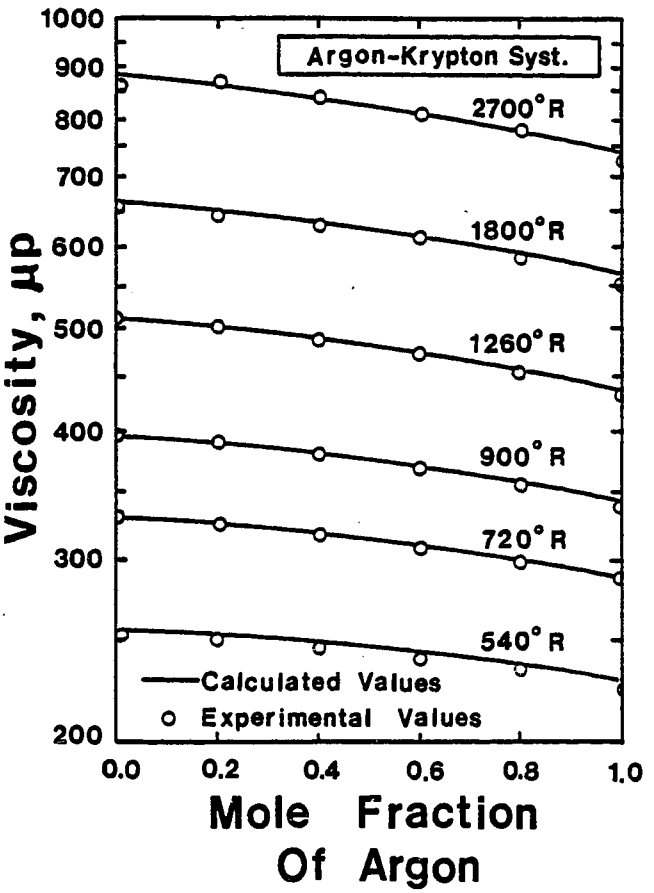

Figure 4.1 Comparison between correlation (Method B) and the experimental Ar-Kr dilute gas mixture viscosity data of Kestin (64).

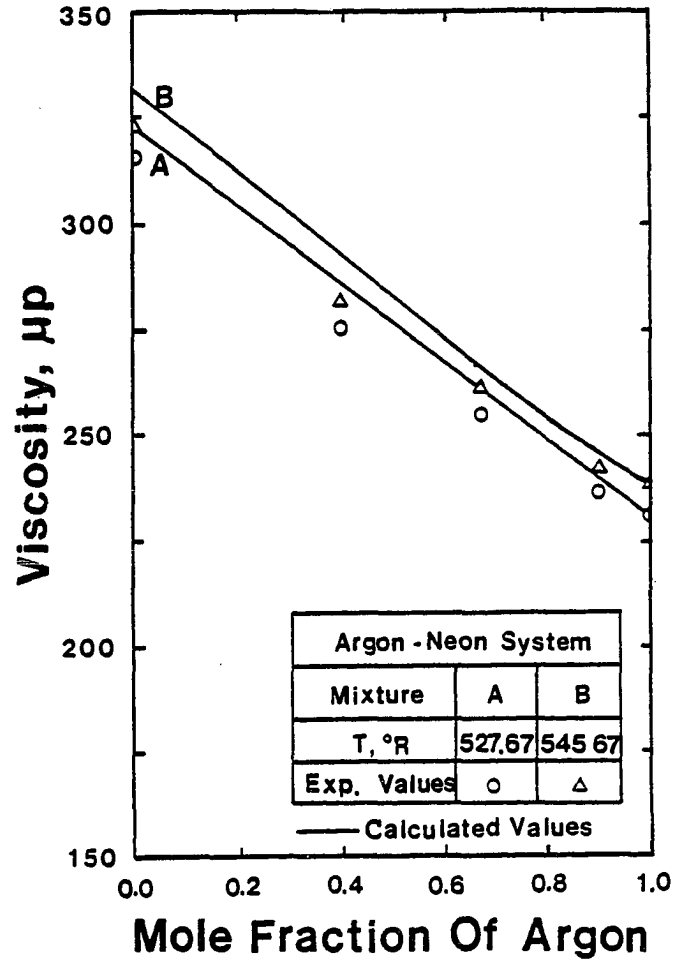

Figure 4.2 Comparison between correlation (Method B) and the experimental Ar-Ne dilute gas mixture viscosity data of Kestin (62).

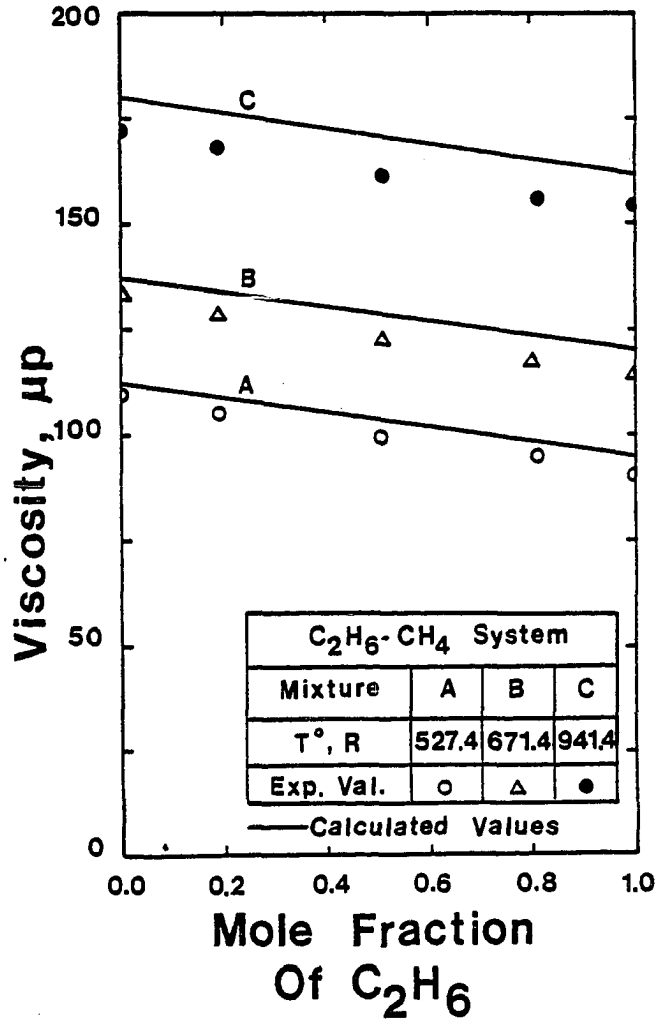

Figure 4.3 Comparison between correlation (Method B) and experimental C_2H_6-CH_4 dilute gas mixture viscosity data of Trautz (122).

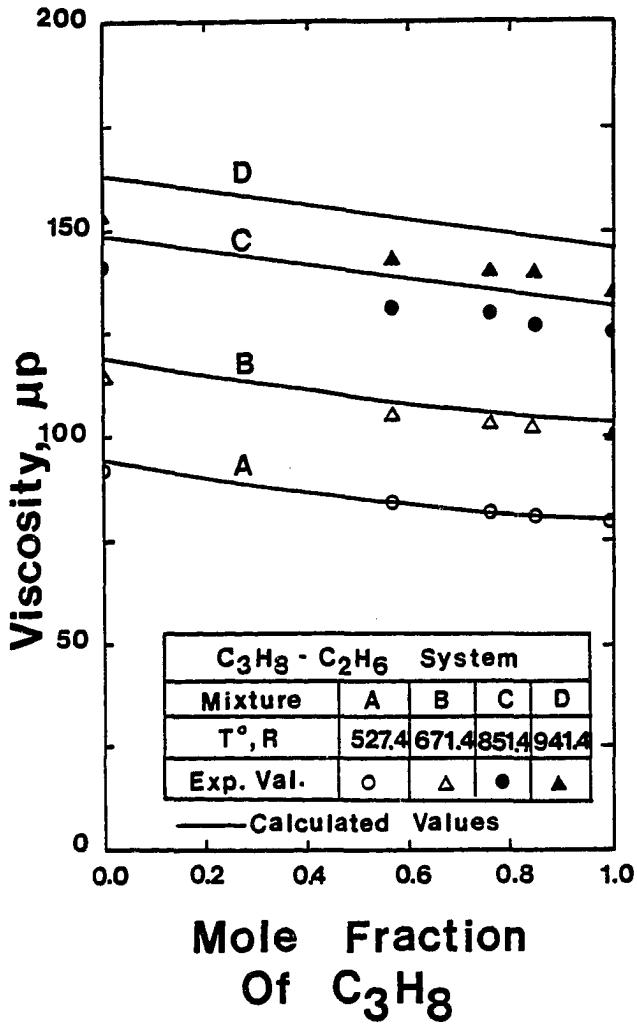

Figure 4.4 Comparison between correlation (Method B) and experimental C_3H_8-C_2H_6 dilute gas mixture viscosity data of Trautz (122).

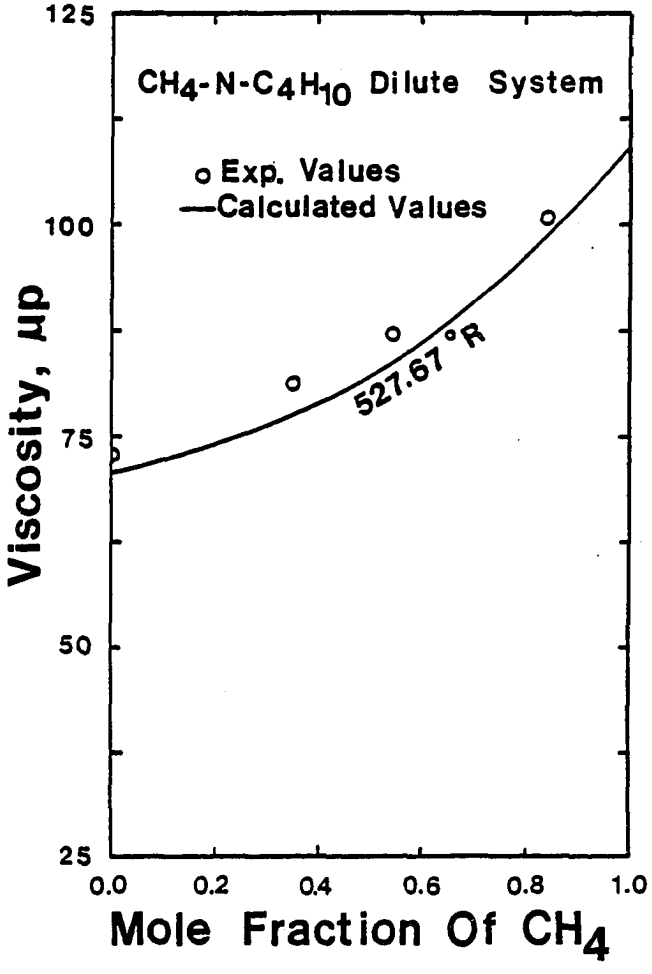

Figure 4.5 Comparison between correlation (Method B) and experimental CH_4-nC_4H_8 dilute gas mixture viscosity data of Kestin (63).

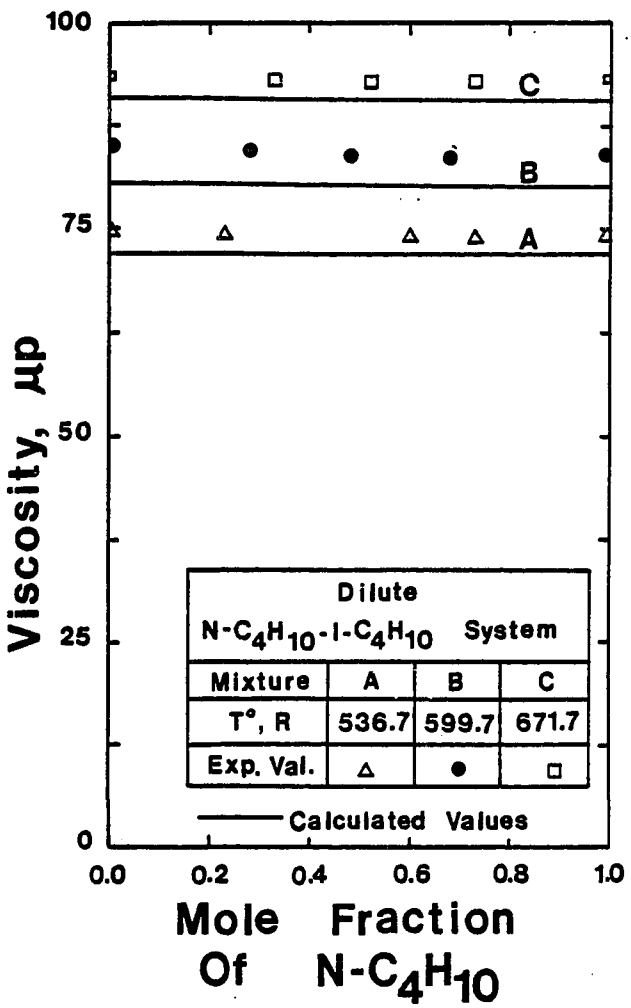

Figure 4.6 Comparison between correlation (Method B) and experimental nC_4H_{10}-iC_4H_{10} dilute gas mixture viscosity data of Abe (1).

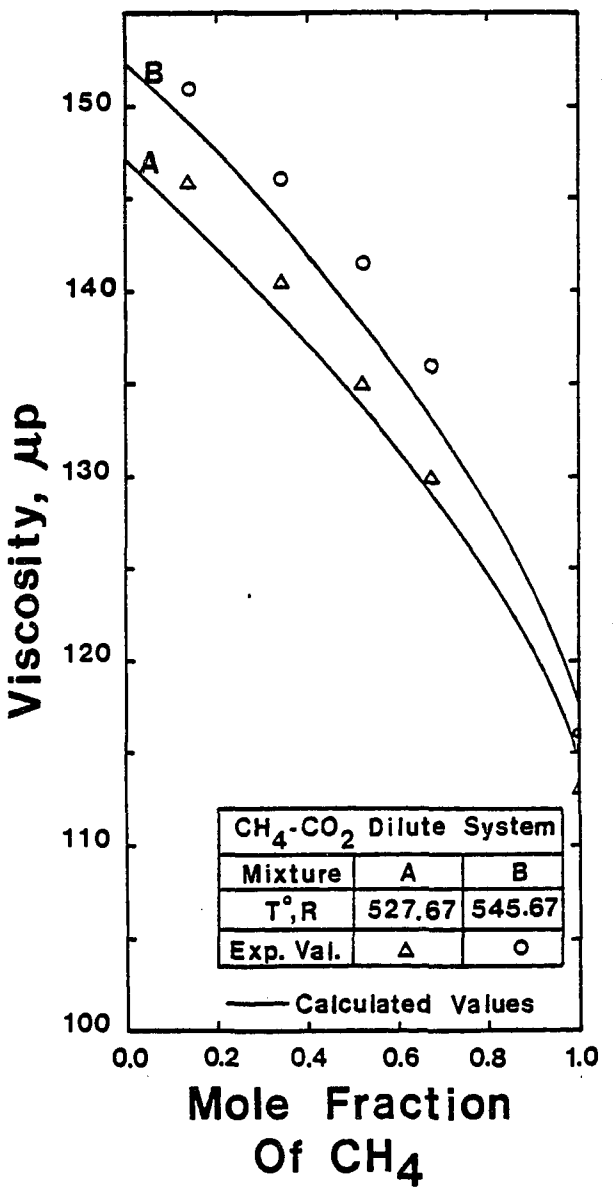

Figure 4.7 Comparison between correlation (Method B) and experimental CH_4-CO_2 dilute gas mixture viscosity data of Kestin (63).

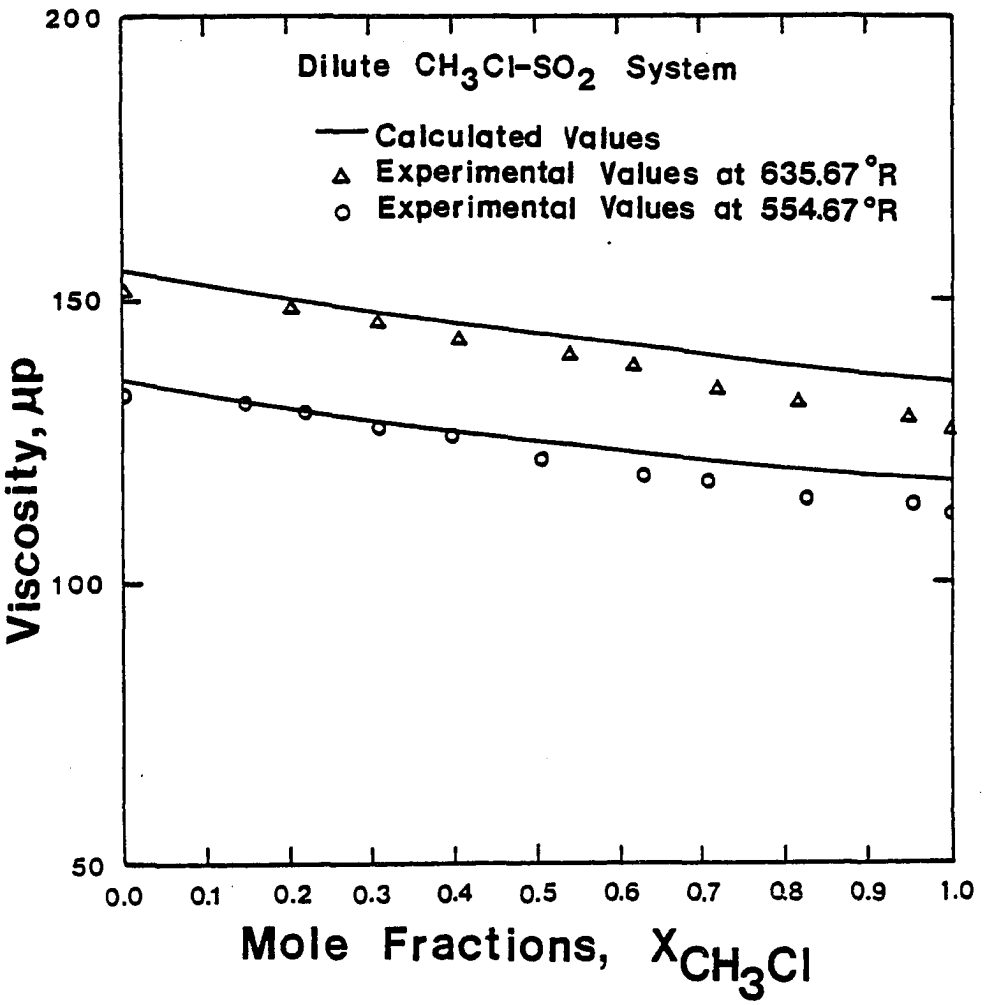

Figure 4.8 Comparison between correlation (Method B) and experimental CH_3Cl-SO_2 dilute gas mixture viscosity data of Chakraborti (14).

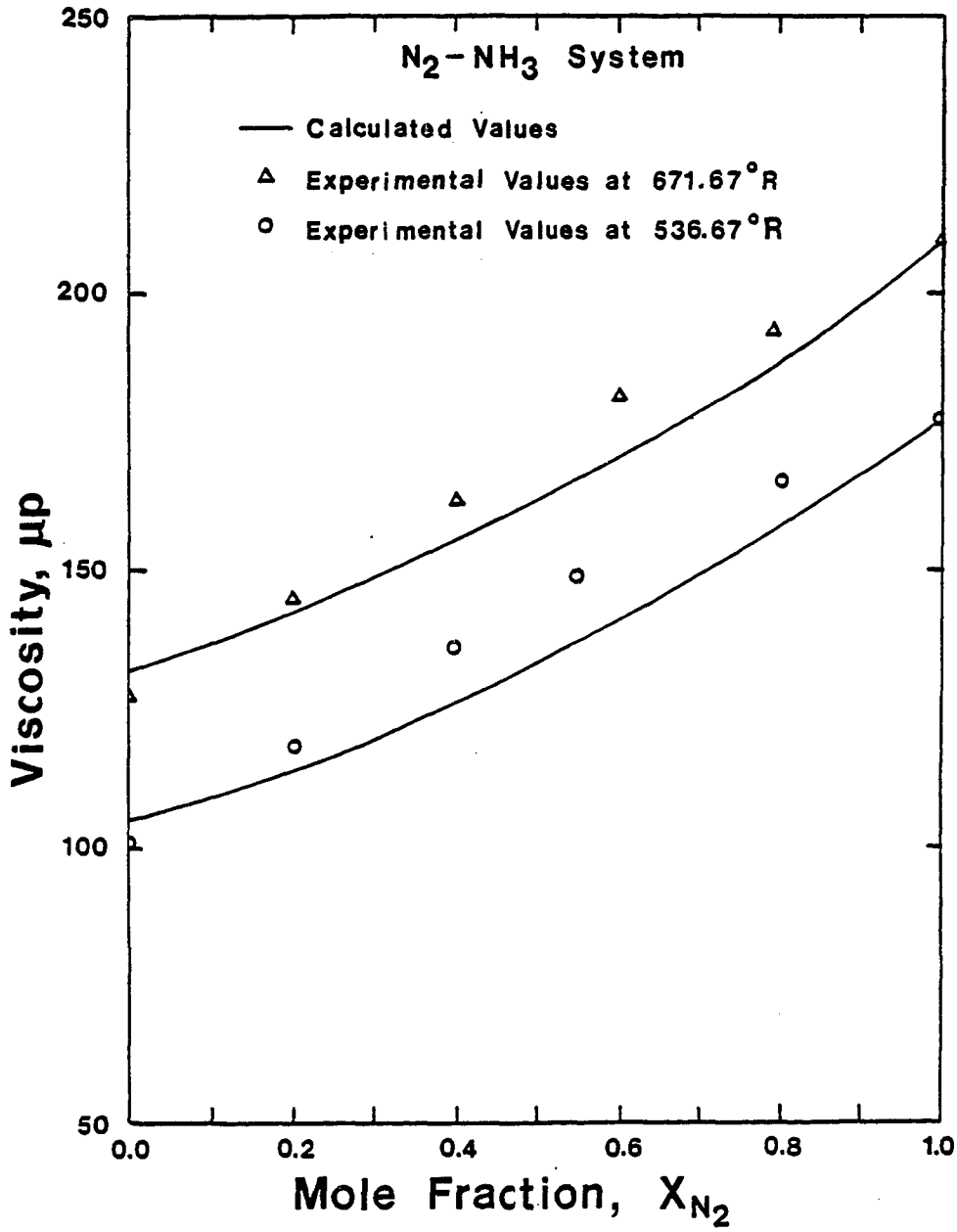

Figure 4.9 Comparison between correlation (Method B) and experimental N_2-NH_3 dilute gas mixture viscosity data of Hongo (48).

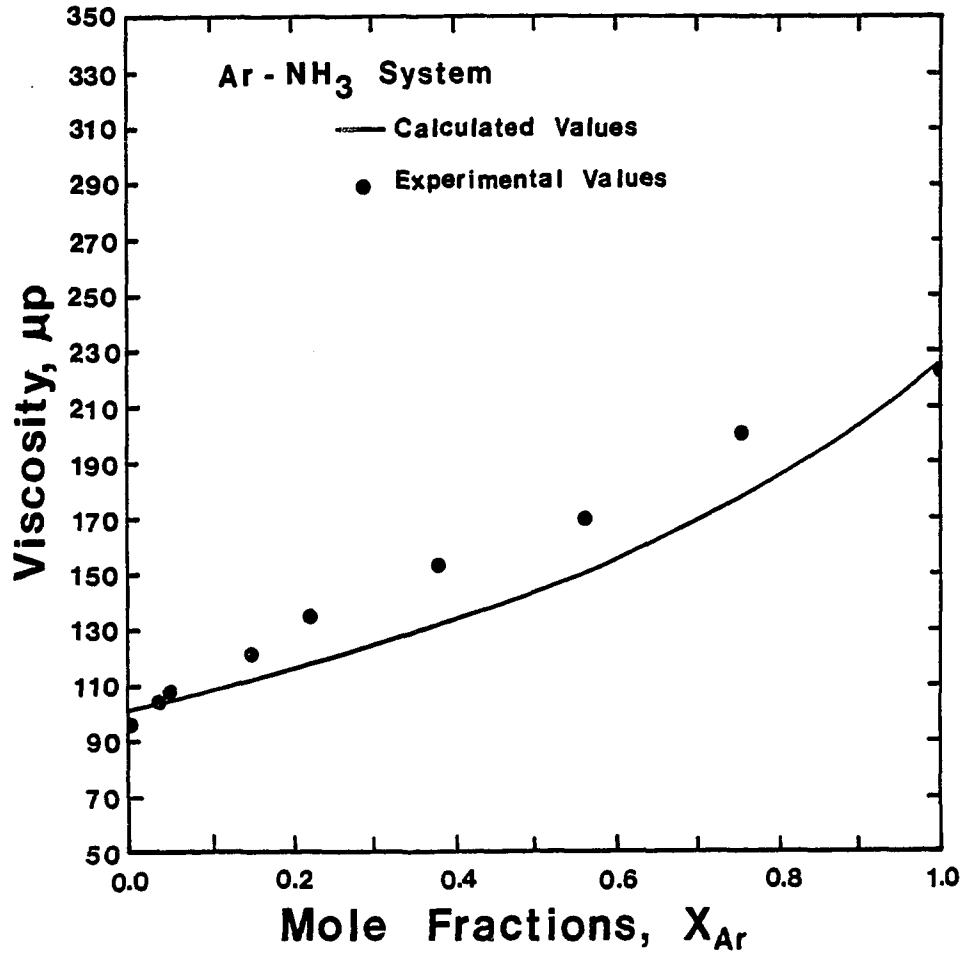

Figure 4.10 Comparison between correlation (Method B) and experimental Ar-NH_3 dilute gas mixture viscosity of Iwasaki (54).

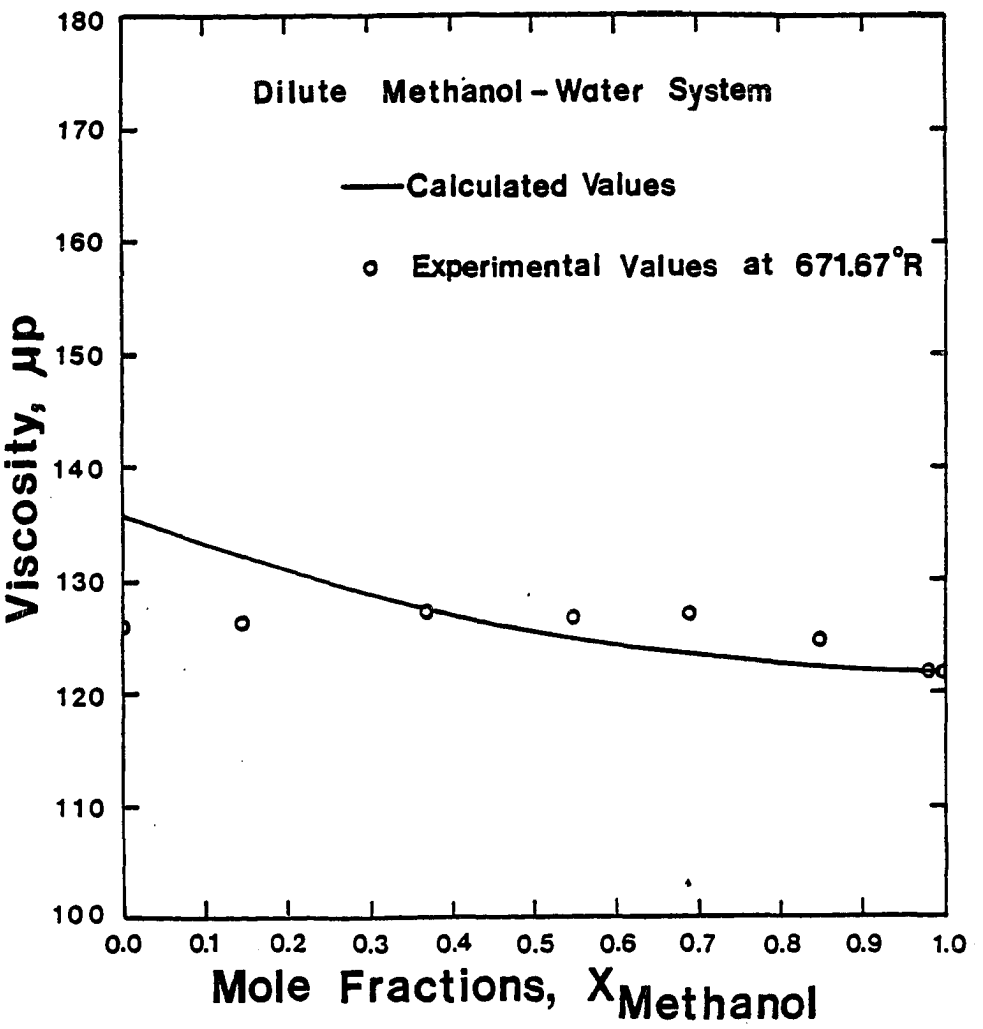

Figure 4.11 Comparison between correlation (Method B) and experimental Methanol-Water dilute gas mixture viscosity data of Silgadro (106).

will represent results obtained by unity interaction parameters (I), interaction parameters from thermodynamics (II) and interaction parameters from experimental viscosity data (III).

It was not necessary to correct the parameter ε_{ij}. Therefore, the interaction parameter corresponding to ε_{ij}, namely ζ_{ij} in equation (3.2.15) was assigned unity value in case III and only a value for ξ_{ij} in equation (3.2.14) was determined from experimental viscosity data. The fact that nonunity values for the binary interaction parameter ξ_{ij} provides improvement in viscosity predictions is a general result which applies to all categories of mixtures studied. The reason is that, for dense gas and liquid mixtures, viscosity is strongly a function of reduced density, which is varied by variation in ξ_{ij}. Thus, the determination of ξ_{ij} from experimental viscosity data may be compensation for errors in density.

To substantiate this conclusion, the viscosities of several mixtures were predicted by calculating the densities using the Hankinson-Thomson (HT) correlation and the results were compared to those predicted by using experimental densities. Predictions for the system $nC_{16} + nC_6$ of Heric (47) produced AAD's of 23.50% when HT correlation was used compared to 19.47% when experimental densities were used.

Predictions for the system benzene + iC_7 of Trevoy (123) produced AAD's of 13.67% and 3.32%, respectively and the system benzene + C_7 of Trevoy followed the same trend and produced AAD's of 11.63% and 7.77%, respectively. All the above results were produced using method B with unity binary interaction parameters. This shows that accurate density values are required for accurate viscosity predictions which in turn requires an accurate equation of state.

For dense gas and liquid mixtures, viscosities for 1,585 points were predicted and compared with experimental values. The results are summarized in Table 4.6. For case I and AAD of 9.19% was obtained by method A and 8.92% was obtained by method B. This accuracy looks quite reasonable considering that no binary interaction parameters are needed. In fact, many systems produced much better AAD than the overall AAD shows. Those systems were the ones with similar molecular size constituents such as methane + propane, methane + n-butane, n-butane + i-butane, etc. The systems which produced large AAD were those with mixture constituents with dissimilar molecular sizes, such as methane + n-decane, methane + n-noname, n-Hexane + n-hexadecane, etc.

The dissimilarity in size will contribute to large differences in the critical volumes, v_{ci}'s, of the mixture constituents and since the characteristic separation parameter σ_i is directly related to v_{ci}, this will lead to

Table 4.6 Summary of Results For The Viscosity of Dense Gas And Liquid Nonpolar Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
CH_4-C_3H_8	468	3.60	--	--	3.73	3.56	--	Lee (67)
CH_4-C_3H_8	140	8.59	6.76	--	6.94	5.95	--	Huang (53)
CH_4-nC_4H_{10}	118	4.03	--	--	4.06	--	--	Lee (67)
CH_4-$nC_{10}H_{22}$	71	34.55	7.08	--	29.19	8.55	--	Lee (68)
CH_4-$nC_{10}H_{22}$	29	25.99	7.66	--	18.78	8.62	--	Bagzis (2)
CH_4-CO_2	132	2.89	--	--	3.97	--	--	DeWitt (22)
CH_4-CF_4	192	7.79	--	5.86	11.42	--	6.73	DeWitt (23)
CH_4-nC_6H_{14}	4	14.86	13.57	--	10.61	9.26	--	Bagzis (2)
CH_4-nC_9H_{20}	32	22.89	6.61	--	13.35	6.85	--	Bennett (9)
$C_2H_6$$nC_{10}H_{22}$	18	26.73	--	6.88	20.80	--	6.44	Bagzis (2)
H_2-CH_4	219	7.05	--	--	8.50	--	--	Chuang (16)
Naphthalene-Benzene	10	7.57	--	--	7.91	--	--	Cambell (13a)
$nC_{16}H_{34}$-nC_6H_{14}	20	27.34	--	2.63	19.47	--	2.72	Heric (47)
$nC_{16}H_{34}$-nC_6H_{14}	2	35.73	--	9.37	28.85	--	9.46	Dixon (24)
$nC_{14}H_{30}$-nC_6H_{14}	10	15.13	--	2.58	10.08	--	2.45	Heric (47)
Benzene-$nC_{16}H_{34}$	9	44.66	--	5.48	35.37	--	4.38	Heric (47)
Benzene-$nC_{16}H_{34}$	6	47.12	--	4.33	34.57	--	3.43	Trevoy (123)

Table 4.6 (Continued)

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Benzene-$nC_{12}H_{26}$	3	3.56	--	1.68	20.49	--	1.31	Trevoy (123)
Benzene-$nC_{14}H_{30}$	3	37.54	--	2.24	25.42	--	1.89	Trevoy (123)
Benzene-$nC_{18}H_{38}$	3	53.12	--	3.54	39.94	--	3.19	Trevoy (123)
$nC_{16}H_{34}$-$nC_{14}H_{30}$	11	4.14	--	--	3.84	--	--	Heric (47)
nC_7H_{16}-$nC_{14}H_{30}$	3	11.15	--	0.51	5.85	--	0.31	Trevoy (123)
nC_7H_{16}-$nC_{16}H_{34}$	3	23.32	--	1.57	16.22	--	1.34	Trevoy (123)
nC_7H_{16}-$nC_{18}H_{38}$	3	29.57	--	2.73	20.50	--	2.52	Trevoy (123)
nC_7H_{16}-$nC_{12}H_{26}$	6	34.60	--	0.70	44.09	--	0.64	Trevoy (123)
iC_7H_{16}-$nC_{12}H_{26}$	3	14.76	--	0.32	22.21	--	0.15	Trevoy (123)
iC_7H_{16}-$nC_{16}H_{34}$	3	31.48	--	0.98	25.98	--	0.80	Trevoy (123)
Benzene-$nC_{10}H_{22}$	3	14.00	--	--	4.61	--	--	Trevoy (123)
Benzen-iC_7H_{16}	3	6.03	--	--	3.32	--	--	Trevoy (123)
Benzene-nC_7H_{16}	3	3.81	--	--	7.77	--	--	Trevoy (123)
Benzene-nC_6H_{14}	10	5.93	--	--	5.89	--	--	Heric (47)
CCl_4-nC_6H_{14}	8	14.76	--	--	14.02	--	--	Heric (47)

Table 4.6 (Continued)

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Benzene-CCl_4	9	28.35	--	--	28.30	--	--	Heric (47)
Toluene-nC_8H_{18}	28	14.47	--	6.93	15.96	--	6.75	Ling (73)
Overall	1585	9.19	--	--	8.92	--	--	

†Avg. Abs. Dev. % = $[\Sigma|(\eta_{exp} - \eta_{cal})/\eta_{exp}|]$ X 100/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

**Binary interaction parameters are taken from thermodynamics

***Binary interaction parameters are determined from viscosity experimental data

larger differences between the σ_i's of the mixture constituents. As a direct result, the unlike pair characteristic separation parameter σ_{ij} obtained by the geometric average of σ_i and σ_j has to be corrected by the binary parameter ξ_{ij}.

To reduce the AAD, the interaction parameters ξ_{ij} and ζ_{ij} were obtained when available from the thermodynamic literature (II) and inserted in equations (3.2.14) and (3.2.15) to correct for σ_{ij} and ε_{ij}. In most of the systems predicted by this approach, the AAD improved considerably. For instance, in the case of the system methane+n-decane, the AAD went down from 34.55% to 7.08% by method A. These results demonstrate the value of self-consistancy between the transport properties and the thermodynamic properties. Also, this suggests that unique values for the binary interaction parameters ξ_{ij} and ζ_{ij} can be obtained by simultaneous regression of experimental data for both thermodynamic and transport properties.

As mentioned above, if the values of ξ_{ij} and ζ_{ij} were not available from thermodynamics, then regression on experimental viscosity data was performed to obtain ξ_{ij}, keeping $\zeta_{ij} = 1.0$. The results by this approach are tabulated in column III of Table 4.6. The AAD improved considerably by this approach. As an example, the AAD for the system benzene + n-hexadecane went down from 47.12%

to 4.33%, as shown in Table 4.6.

Because it was very difficult to find experimental data in the literature for polar-nonpolar liquid mixtures, only one system, the benzene + benzonitrile system, was found as shown in Table 4.7. For this system of 9 points, the viscosity was predicted with an AAD of 21.21% and 21.75% by methods A and B, respectively. No improvement in the accuracy was obtained when binary interaction parameters were introduced. It is impossible to draw conclusions from this study for this single system and until more experimental data are available, the predictive capability of the correlation for this class of mixtures remains in doubt.

Results for binary liquid mixtures with association effects are presented in Table 4.8. For a total of 521 points, the viscosity was predicted and compared with experimental data. The overall AAD was higher than for the previously discussed mixtures when the binary interaction parameters were taken to be of unity. As shown in column I of Table 4.8, an AAD of 24.06% was achieved by method A, and 22.81% by method B. Determining the binary interaction parameter ξ_{ij} and keeping the other binary parameter ζ_{ij} equal to unity, the AAD considerably improved for most of the systems, as is shown in column III of Table 4.8.

Table 4.9 presents the prediction results for binary liquid mixtures with association and nonpolar effects. Not

Table 4.7 Summary of Results For The Viscosity of Liquid Nonpolar-Polar Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Benzene-Benzonitrile	9	21.21	--	--	21.75	--	--	Reddy (97)

†Avg. Abs. Dev. % = $[\Sigma|\ (\eta_{exp} - \eta_{cal})/\eta_{exp}|]$ X 100/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

**Binary interaction parameters are taken from thermodynamics

***Binary interaction parameters are determined from viscosity experimental data

Table 4.8 Summary of Results For The Viscosity of Liquid Associated-Associated Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Methanol-Water	156	22.67	--	13.04	22.20	--	13.19	Kubota (65)
Methanol-Water	60	28.81	--	14.03	26.41	--	14.43	Mikhail (83)
Ethanol-Water	87	44.23	--	14.81	43.35	--	13.84	Tanak (116)
n-Propanol-Water	19	44.05	--	--	42.03	--	--	Ling (73)
Acetone-Water	93	22.22	--	--	19.88	--	--	Howard (51)
Acetone-Acetic Acid	11	13.04	--	1.41	13.13	--	1.40	Howard (52)
4-Methyl-2-Pentone-Acetic Acid	44	15.84	--	0.74	11.70	--	1.15	Hafez (43)
4-Butanol-Methyl-Isobutyl Ketone	41	8.58	--	5.95	9.84	--	5.81	Dakshinamurty (20)
Tetrahydrofuran-Water	10	31.17	--	12.24	29.58	--	11.53	Hayduk (46)
Overall	521	25.95	--	--	24.61	--	--	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

**Binary interaction parameters are obtained from thermodynamics

***Binary interaction parameters are obtained from experimental transport data

Table 4.9 Summary of Viscosity Results For Nonpolar-Associated Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Benzene-Acetone	11	6.56	--	--	6.38	--	--	Howard (52)
Benzene-Methyl Ethyl Ketone	53	26.41	--	20.36	26.38	--	20.31	Teller (118)
Benze-Methyl Propyl Ketone	10	16.06	--	--	15.91	--	--	Reddy (97)
Overall	74	22.06	--	--	22.00	--	--	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

**Binary interaction parameters are obtained from thermodynamics

***Binary interaction parameters are obtained from experimental transport data

too many experimental systems were available in the literature and only 74 data points were found. The AAD for two of the three mixture systems are acceptable with unity binary interaction parameters. However, the system benzene + methyl ethyl ketone produced a somewhat high AAD by both method A and B. Actually, the AAD did not improve by the introduction of the binary interaction parameters. An overall AAD of 22.06% and 22.00% were produced by method A and B, respectively.

Table 4.10 presents the prediction results for binary liquid mixtures with association and polar effects. Only 62 data points were found in the literature. The overall AAD produced was 8.14% and 7.68% by method A and B, respectively. While only a few data points were tested, the AAD is acceptable with unity binary interaction parameters.

A total of 2,251 dense gas and liquid mixture points were predicted and the overall AAD achieved when the binary interaction parameter were taken to have unity values were 13.47% and 12.96% by methods A and B, respectively. Of course the deviations improve considerably when binary interaction parameters are introduced.

Including all the mixture systems, with a total of 3,312 viscosity points, the overall average absolute deviation is 10.57% and 10.14% for method A and B, respectively.

Comparison between experimental and predicted viscosities for some selected dense gas and liquid systems are illustrated graphically in Figures 4.11 through 4.20.

Table 4.10 Summary of Viscositv Results For Polar-Associated Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Toluene-Acetone	44	6.81	--	--	6.23	--	--	Hafez (43)
Chloroform-Acetic Acid	18	11.37	--	5.95	11.22	--	5.94	Vitagliano (128)
Overall	62	8.14	--	--	7.68	--	--	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

**Binary interaction parameters are obtained from thermodynamics

***Binary interaction parameters are obtained from experimental transport data

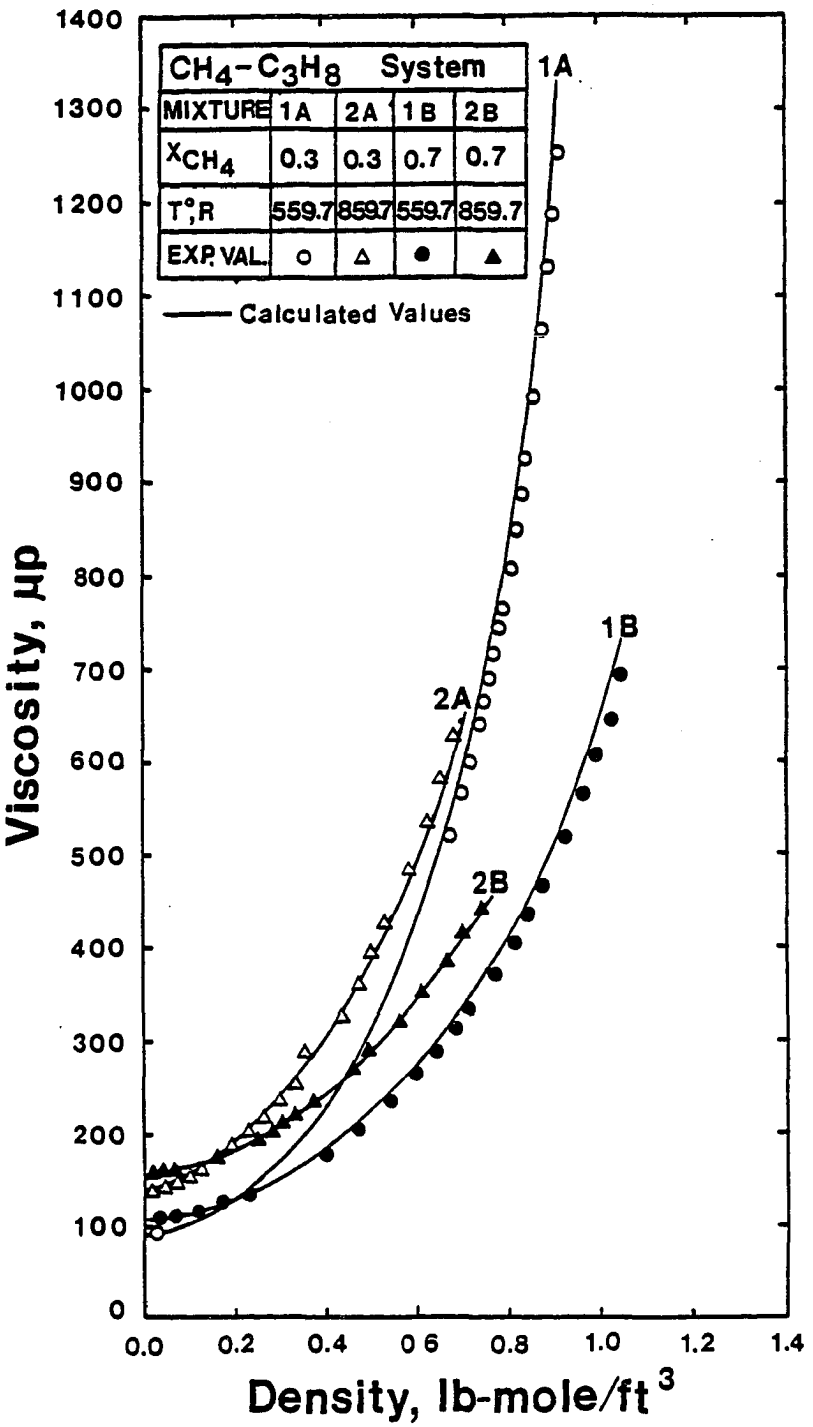

Figure 4.12 Comparison between correlation (Method B) and experimental $CH_4-C_3H_8$ dense gas mixture viscosity data of Lee (67).

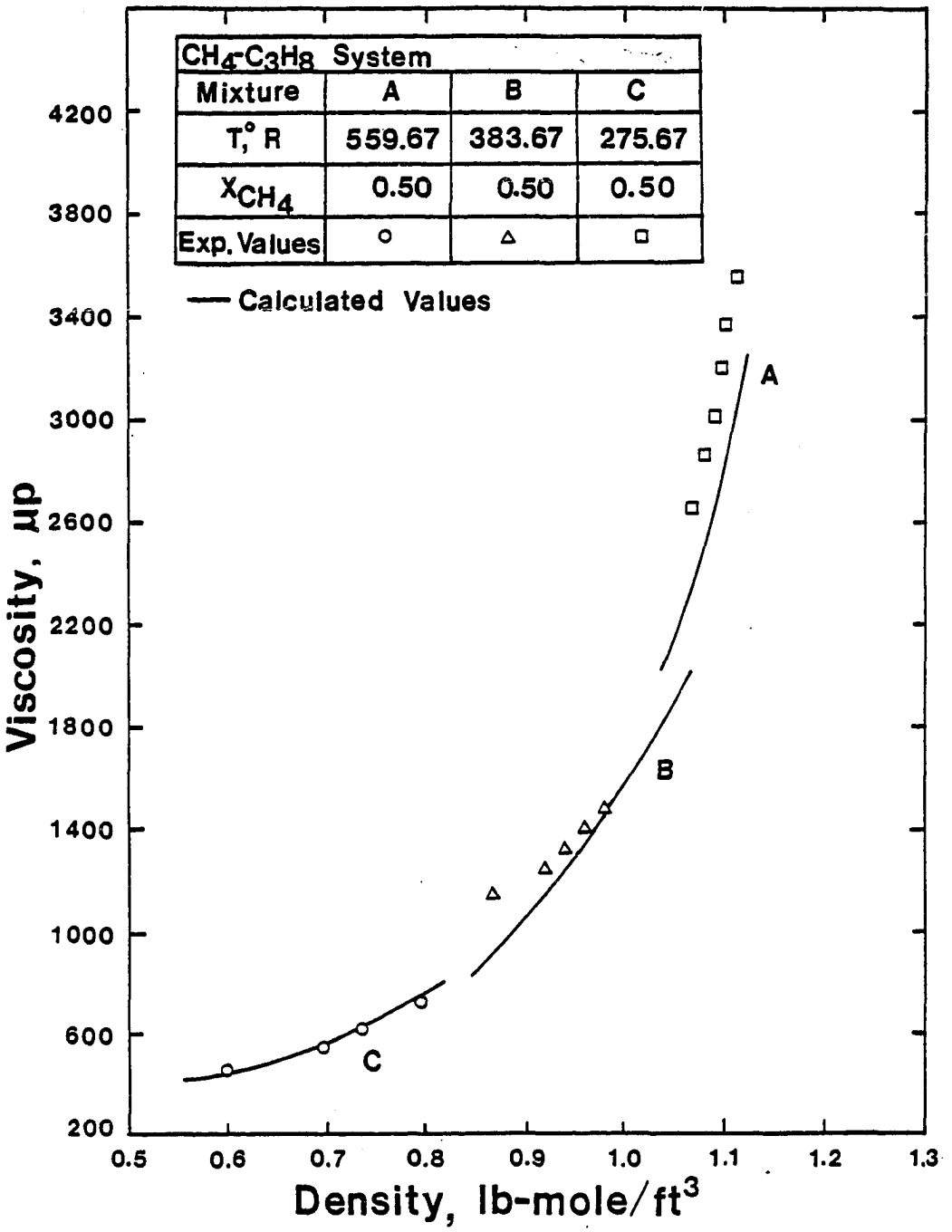

Figure 4.13 Comparison between correlation (Method B) and experimental CH_4-C_3H_8 dense gas mixture viscosity data of Huang (53).

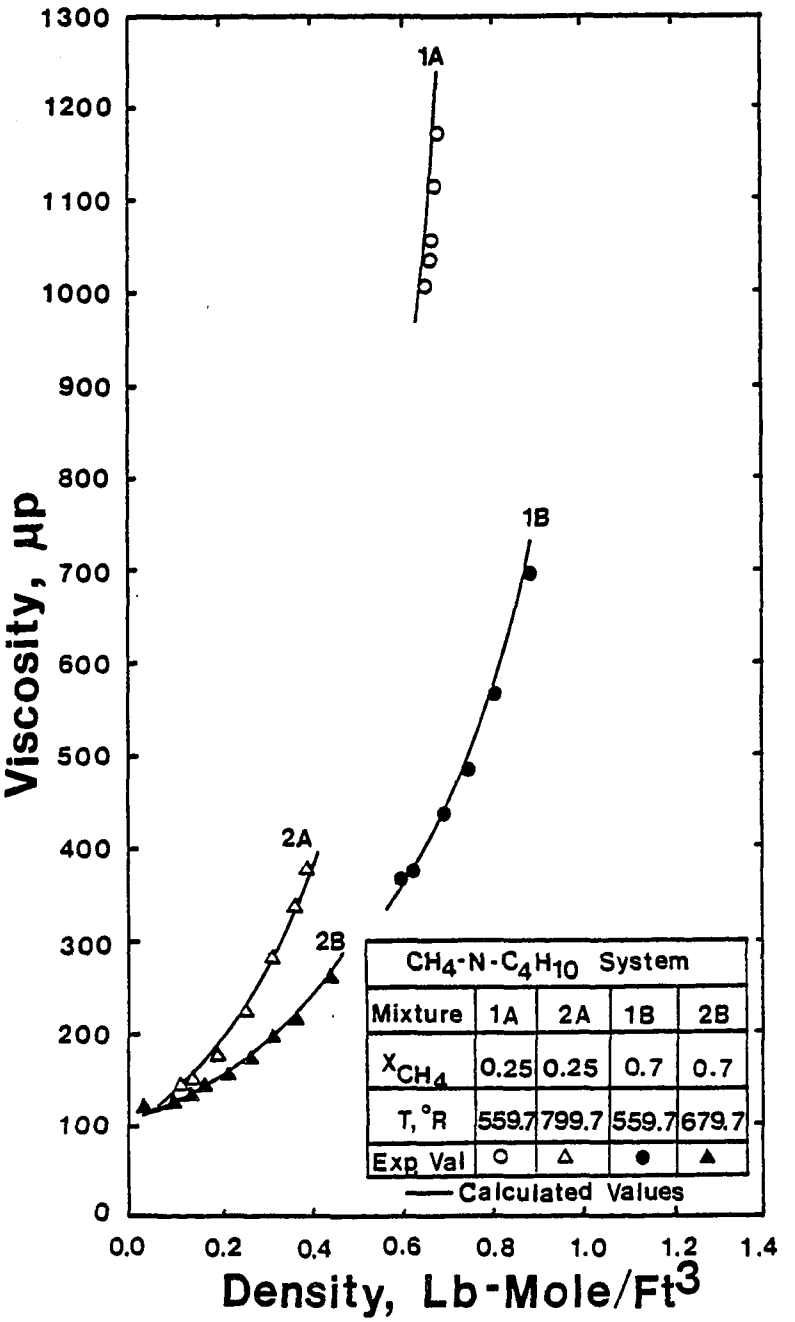

Figure 4.14 Comparison between correlation (Method B) and experimental CH_4-nC_4H_{10} dense gas mixture viscosity data of Lee (67).

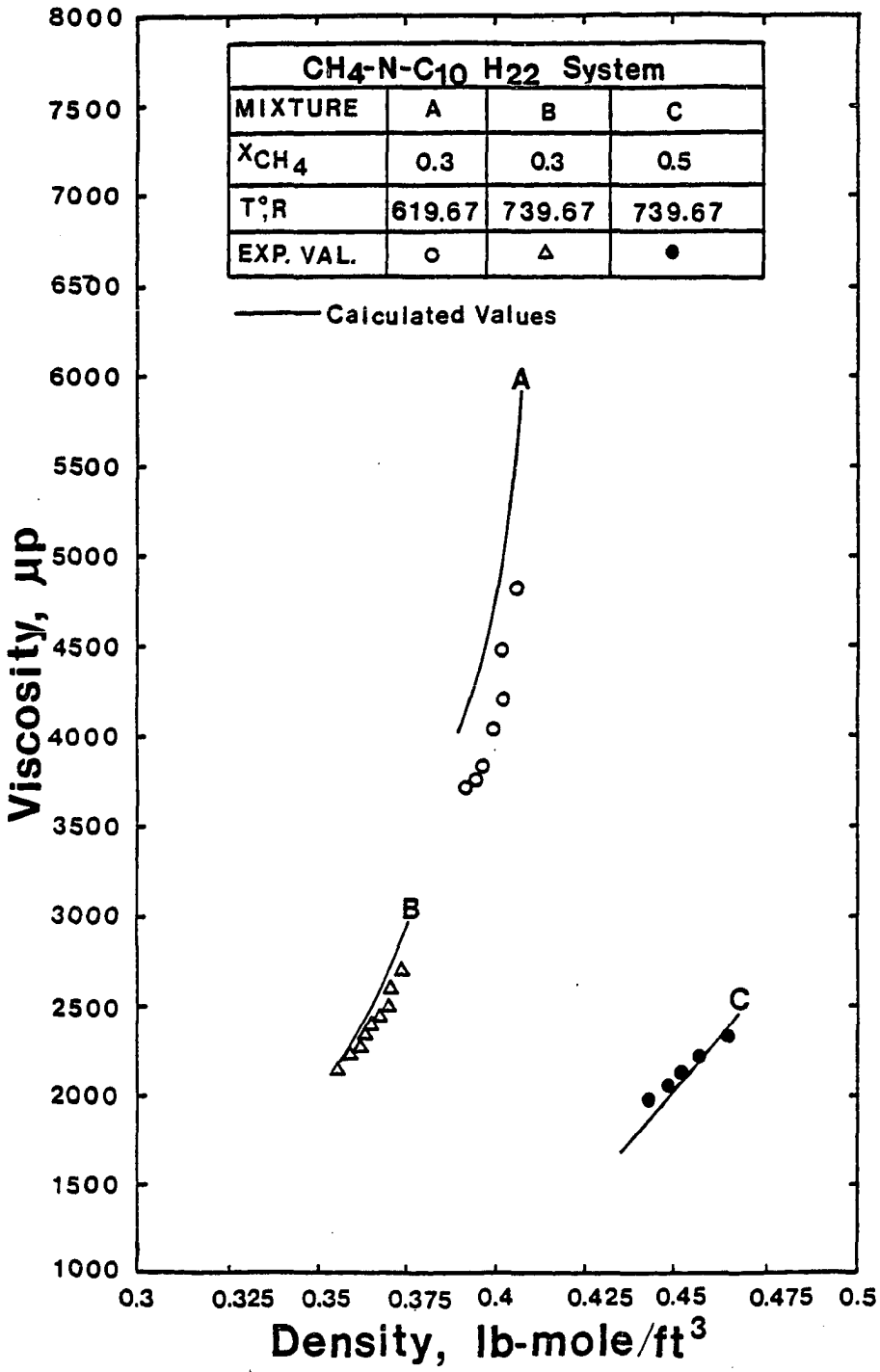

Figure 4.15 Comparison between correlation (Method B) and experimental CH_4-$nC_{10}H_{22}$ dense gas mixture viscosity data of Lee (68).

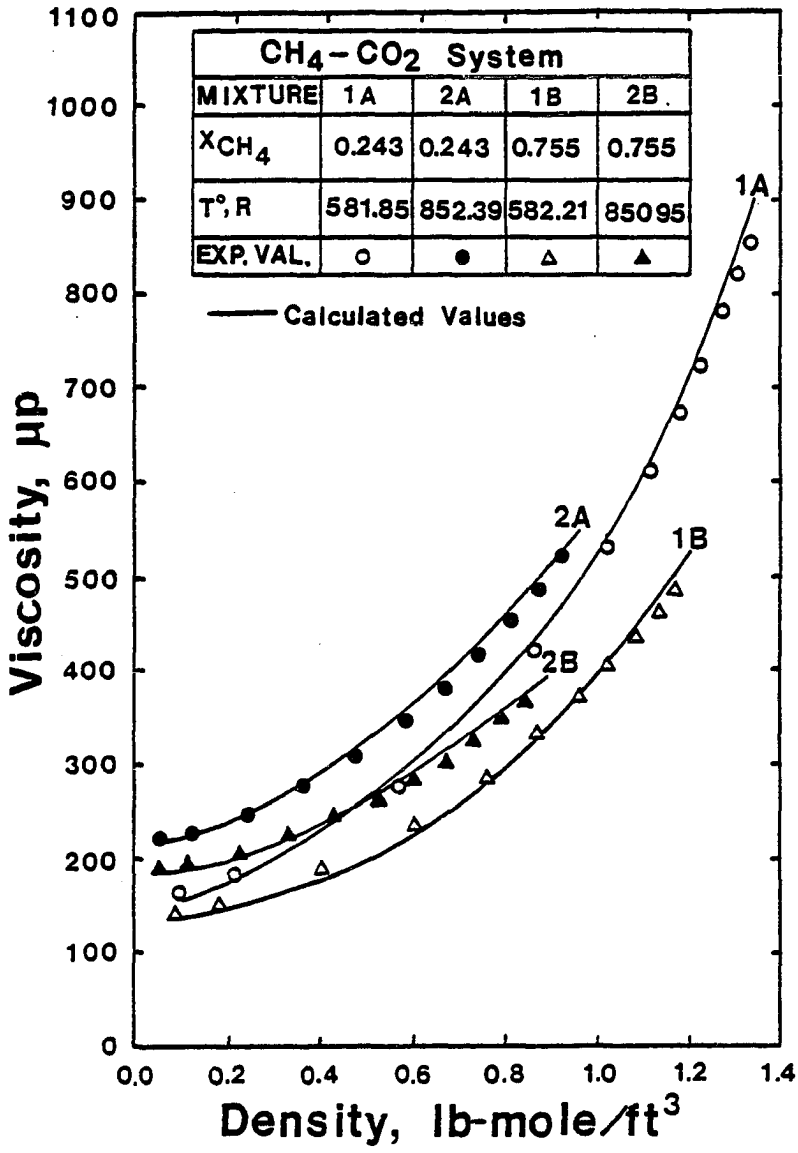

Figure 4.16 Comparison between correlation (Method B) and experimental CH_4-CO_2 dense gas mixture of viscosity data of DeWitt (22).

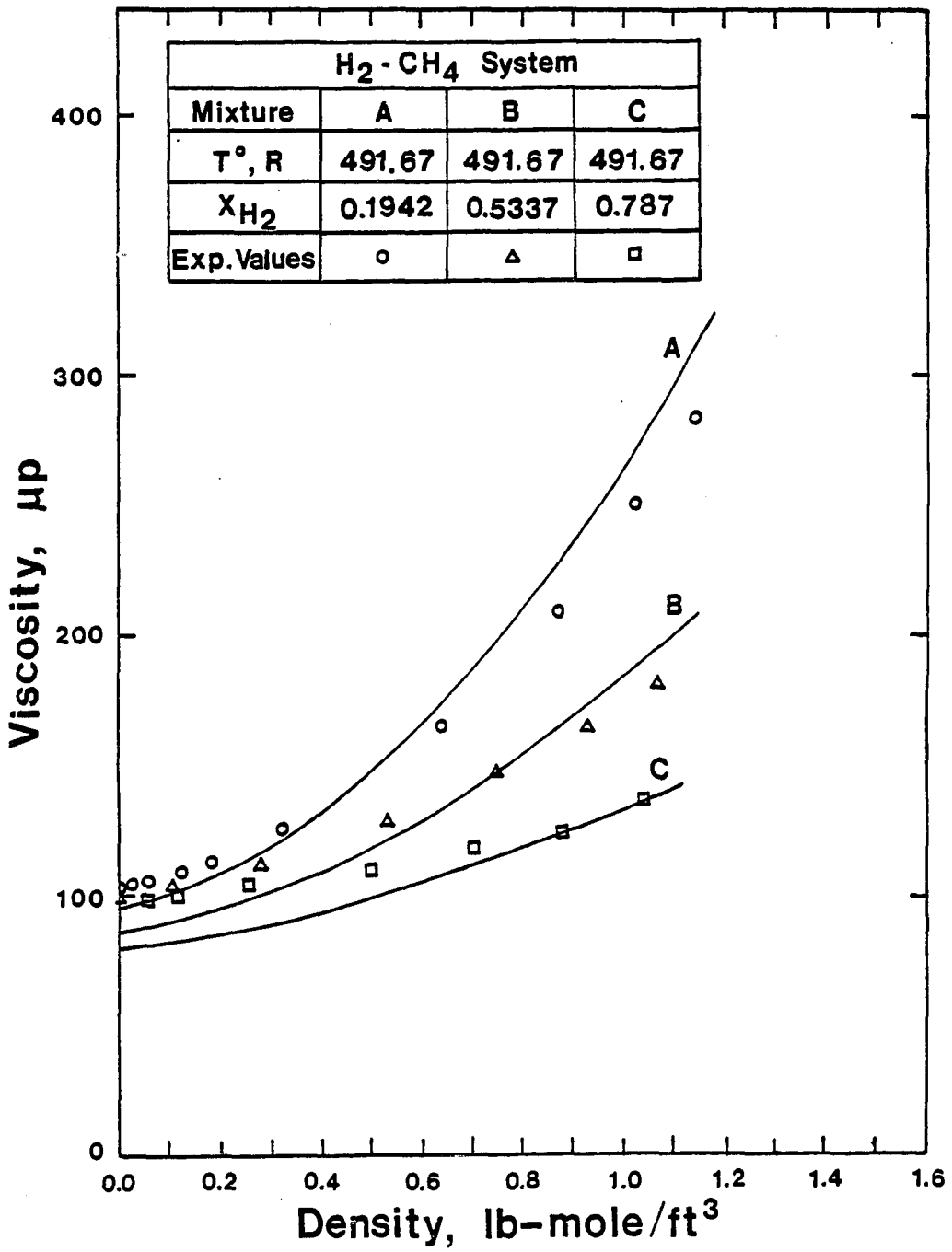

Figure 4.17 Comparison between correlation (Method B) and experimental H_2-CH_4 dense gas mixture viscosity data of Chuang (16).

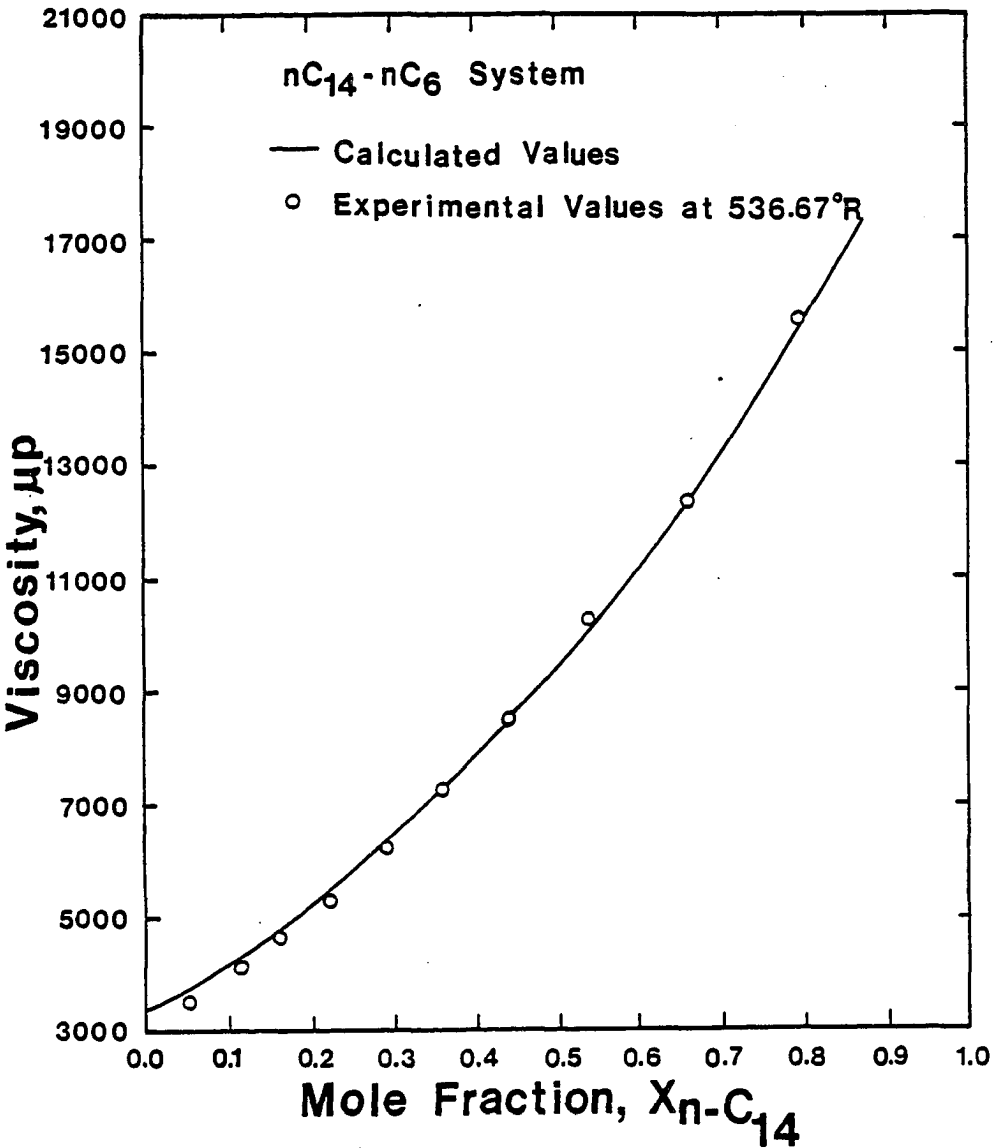

Figure 4.18 Comparison between correlation (Method B) and experimental nC_{14}-nC_6 liquid mixture viscosity data of Heric (47).

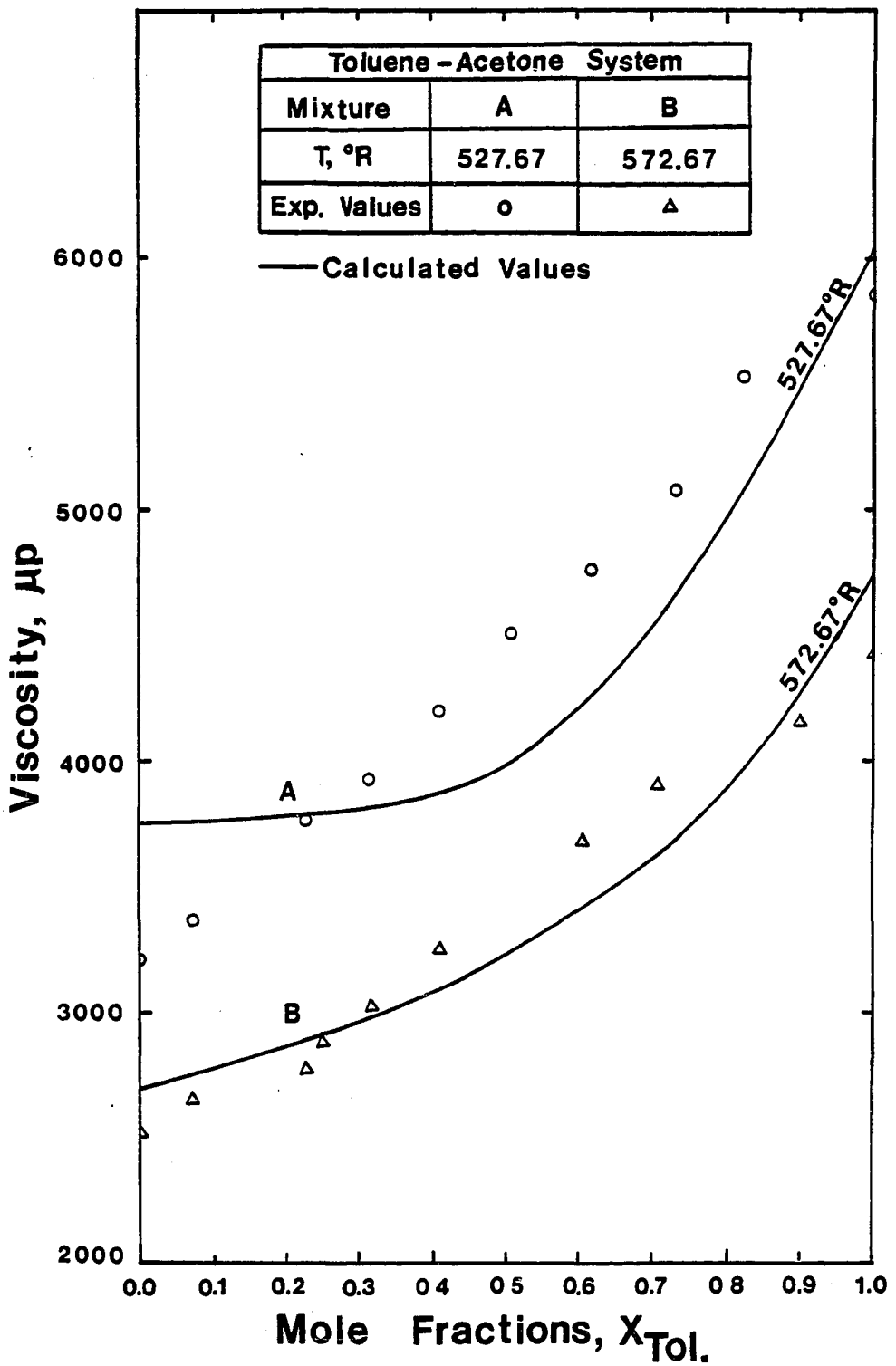

Figure 4.19 Comparison between correlation (Method B) and experimental Toluene-Acetane liquid mixture viscosity data of Hafez (43).

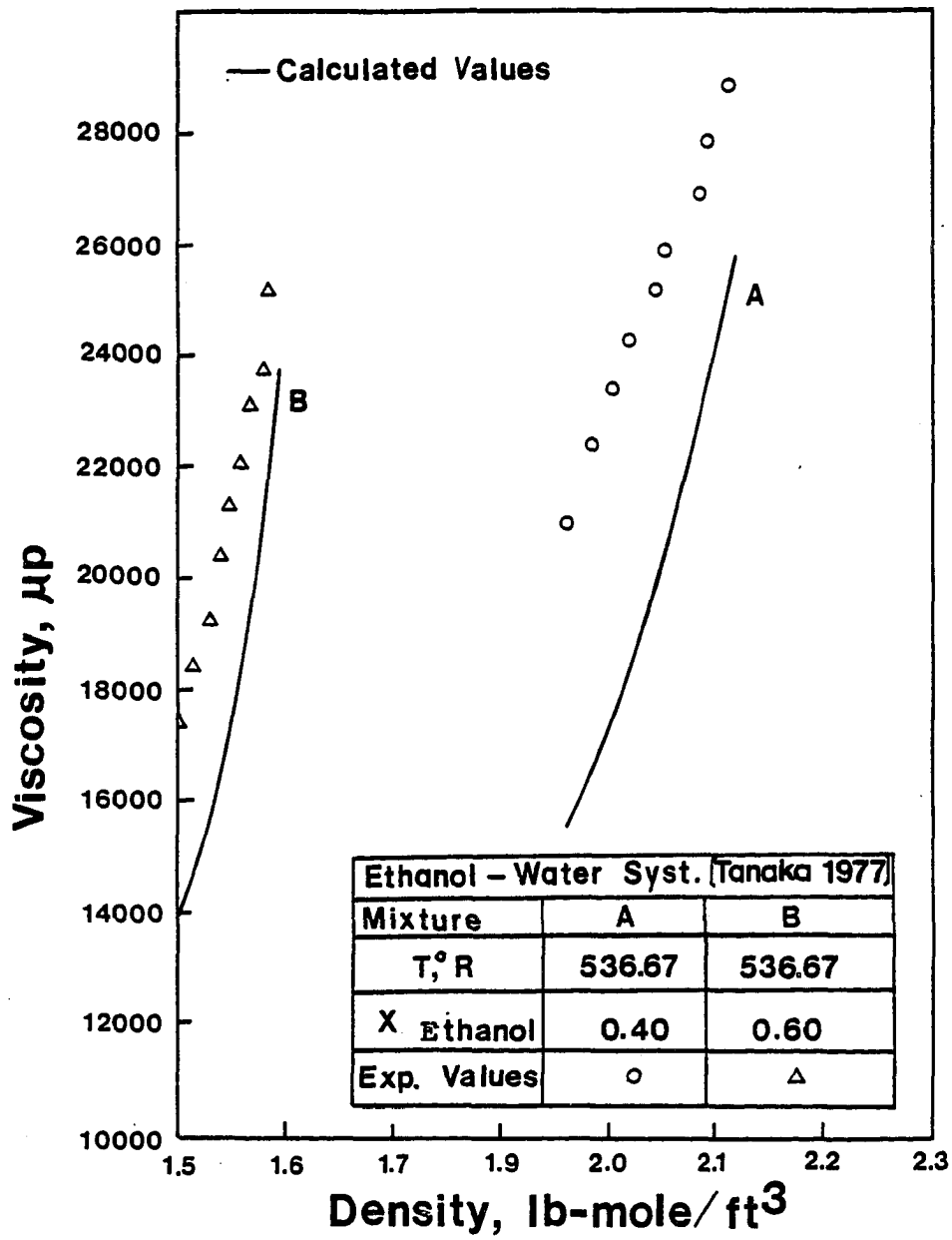

Figure 4.20 Comparison between correlation (Method B) and experimental Ethanol-Water liquid mixture viscosity data of Tanaka (116).

The value of the unlike parameter κ_{ij} used in the viscosity predictions of associated mixtures presented in Tables 4.8 through 4.10 was calculated by the combining rule of equation (3.2.16). The accuracy of prediction was not satisfactory and more accurate combining rule for κ_{ij} was essential to improve the predictions. Therefore, equations (3.2.18a) and (3.2.18b) were used instead of equation (3.2.16) as discussed in Chapter III. Along with the generalized binary interaction parameters of equations (3.2.19) and (3.2.20) for ξ_{ij} and ϕ_{ij}. The results of this approach are presented in Table 4.11 for binary liquid mixtures with association effects, Table 4.12 for binary liquid mixtures with association and nonpolar effects and Table 4.13 for binary liquid mixtures with association and polar effects. The AAD's are 13.53%, 17.21% and 7.24%, respectively, by method A and 13.79%, 17.12% and 9.27%, respectively, by method B. This approach effectively reduced the AAD for most of the cases, especially for binary liquid mixtures with association effects. Comparing the results of column I in Table 4.8 to those of Table 4.11, the AAD went down from 24.06% to 13.53% for method A. The use of equations (3.2.18a) and 2.3.18b) is recommended over the other model of equation (3.2.16) for binary liquid mixtures containing associated compounds. For dilute associated gas mixtures, equation (3.2.16) produces satisfactory results and should be used for this category of mixture.

Table 4.11: Summary of Viscosity Results For Associated-Associated Liquid Mixtures With The Generalized Binary Interaction Parameters

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A	Method B	
Methanol-Water	156	9.79	9.85	Kubota (65)
Methanol-Water	60	13.10	12.72	Mikhail (83)
Ethanol-Water	87	25.62	24.51	Tanaka (116)
n-Propanol-Water	19	28.17	28.85	Ling (73)
Acetone-Water	93	12.55	15.88	Howard (51)
Acetone-Acetic Acid	11	5.91	8.93	Howard (52)
4-Methyl-2 Pentone-Acetic Acid	44	7.28	4.54	Hafez (43)
n-Butanol-Methyl-isobutyl Ketone	41	6.03	6.56	Dakshinamurty (20)
Tetrahydrofuran-Water	10	17.14	15.32	Hyduk (46)
Overall	521	13.53	13.77	

†Avg. Abs. Dev. % = $[\Sigma \frac{\eta_{exp} - \eta_{cal}}{\eta_{exp}} \times 100]$/No. of Points

Table 4.12: Summary of Viscosity Results For Nonpolar-Associated Liquid Mixtures With The Generalized Binary Interaction Parameters

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A	Method B	
Benzene -Acetone	11	6.63	3.02	Howard (52)
Benzene-Methyl Ethyl Ketone	53	21.23	22.20	Teller (118)
Benzen-Methyl Propyl Ketone	10	7.58	5.68	Reddy (97)
Overall	74	17.21	17.12	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100]$/No. of Points

Table 4.13: Summary of Viscosity Results For Polar-Associated Liquid Mixtures With The Generalized Binary Interaction Parameters

Mixtures	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A	Method B	
Toluene-Acetone	44	7.22	8.21	Hafez (43)
Chloroform-Acetic Acid	18	7.27	11.86	Vitagliano (128)
Overall	62	7.24	9.27	

†Avg. Abs. Dev. % = $[\Sigma \frac{\eta_{exp} - \eta_{cal}}{\eta_{exp}} \times 100]$/No. of Points

The conformal solution theory models presented previously as method A and B are powerful and very easily used for the viscosity prediction. But, binary interaction parameters are needed to improve the accuracy of prediction especially for mixtures with greatly different molecular size. These binary interaction parameters are not always available, particularly for new mixture systems. Therefore, to eliminate the need for these parameters, the empirical model presented in section 3.6 is introduced for the viscosity prediction of nonpolar gas mixtures. This approach will be referred to as method C in this Chapter. Table 4.14 compares the results produced by this method with those produced by method A for dilute nonpolar gas mixtures. Results by other methods compare very well in accuracy. Table 4.18 presents the results for nonpolar dense gas and liquid mixtures. For many systems, method C produced better results than the conformal solution theory of method A when binary interaction parameters are taken to have unity values. Of particular interest, the system methane + n-decane of Lee (68) produced an AAD of 12.04% comparied to 34.55% by method A. The overall average absolute deviation improved from 9.19% by method A to 7.22% by method C. Even though this method C is empirical, it works well for many mixtures particularly when the mixture

Table 4.14 Comparison Between This Work And Wilke's Equation (2.1.7) For The Viscosity of Dilute Nonpolar Gas Mixtures

Mixture	No. of Points	AAD %†			Reference
		Method A*	Method C	Wilke's	
Ar-Kr	65	2.57	3.09	1.50	Kestin (64)
Ar-Ne	78	0.79	1.50	2.01	Kestin (62)
CH_4-C_2H_6	20	0.81	1.34	0.74	Trautz (122)
C_2H_6-C_3H_8	20	2.25	2.31	2.24	Trautz (122)
CH_4-nC_4H_{10}	41	0.78	2.57	0.89	Kestin (63)
nC_4H_{10}-iC_4H_{10}	29	0.54	0.42	0.43	Abe (1)
CH_4-CO_2	56	2.96	0.47	1.68	Kestin (63)
Overall	309	1.63	1.73	1.48	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100] \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 4.15 Comparison Between This Work And Wilke's Equation (2.1.7) For The Viscosity of Dilute Polar Gas Mixtures

Mixture	No. of Points	AAD %†		Reference
		Method A*	Wilke's	
CH_3Cl-SO_2	21	2.83	3.23	Chakrabroti (14)
$(CH_3)_2O$-CH_3Cl	21	3.02	2.94	Chakrobroti (14)
$(CH_3))$-SO_2	22	3.95	2.24	Chakrabroti (14)
Overall	64	3.28	2.83	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{cal}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 4.16 Comparison Between This Work And Wilke's Equation (2.1.7) For The Viscosity of Dilute Nonpolar-Polar Gas Mixtures

Mixture	No. of Points	AAD %†		Reference
		Method A*	Wilke's	
$Ar-NH_3$	130	8.61	2.25	Iwasaki (54)
$Ar-NH_3$	32	7.31	3.10	Chakraborti (15)
N_2-NH_3	276	3.87	3.20	Hongo (48)
CH_4-NH_3	33	1.83	2.03	Chakraborti (15)
N_2O-NH_3	33	7.12	1.88	Chakraborti (15)
$Ar-SO_2$	35	3.43	3.69	Chakraborti (15)
N_2O-SO_2	34	2.38	1.97	Chakraborti (15)
CO_2-SO_2	37	2.02	1.65	Chakraborti (15)
CH_4-SO_2	19	2.64	1.23	Chakraborti (15)
N_2-CClF_3	19	3.04	3.11	Tanaka (117)
N_2CHClF_2	21	3.63	2.02	Tanaka (117)
Overall	669	4.75	2.67	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 4.17 Comparison Between This Work And Wilke's Equation (2.1.7) For The Viscosity of Dilute Associated Mixtures

Mixture	No. of Points	AAD %†		Reference
		Method A*	Wilke's	
Methanol-Water	8	2.41	2.49	Silgadro (106)
Ethanol-Water	11	3.92	3.24	Silgadro (106)
Overall	19	3.29	2.92	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 4.18 Comparison Between This Work And The Dean And Stiel Equation (2.1.32) For The Viscosity of Nonpolar Dense Gas And Liquid Mixtures

Mixture	No. of Points	AAD %†			Reference
		Method A*	Method C	Dean & Stiel	
CH_4-C_3H_8	468	3.60	2.84	4.70	Lee (67)
CH_4-C_3H_8	140	8.59	8.97	20.12	Huang (53)
CH_4-nC_4H_{10}	118	4.03	3.05	6.06	Lee (67)
CH_4-$nC_{10}H_{22}$	71	34.55	12.05	45.69	Lee (68)
CH_4-$nC_{10}H_{22}$	29	25.99	8.77	62.96	Bagzis (2)
CH_4-CO_2	132	2.89	1.88	2.89	DeWitt (22)
CH_4-CF_4	192	7.79	4.64	3.22	DeWitt (23)
CH_4-nC_6H_{14}	4	14.86	12.57	39.80	Bagzis (2)
CH_4-nC_9H_{20}	32	22.89	19.66	64.91	Bennett (9)
C_2H_6-$nC_{10}H_2$	18	26.73	15.55	52.33	Bagzis (2)
H_2-CH_4	219	7.05	8.55	7.50	Chuang (16)
Naphthalene-Benzene	10	7.57	11.24	40.57	Cambell (13a)
$nC_{16}H_{34}$-nC_6H_{14}	20	27.34	24.74	72.93	Heric (47)
$nC_{16}H_{34}$-nC_6H_{14}	2	35.73	11.27	74.32	Dixon (24)
$nC_{14}H_{30}$-nC_6H_{14}	10	15.13	23.53	61.46	Heric (47)
Benzene-$nC_{16}H_{34}$	9	44.66	19.02	69.82	Heric (47)
Benzene-$nC_{16}H_{34}$	6	47.12	25.36	72.35	Trevoy (123)
Benzene-$nC_{12}H_{26}$	3	3.56	96.83	50.73	Trevoy (123)
Benzene-$nC_{14}H_{30}$	3	37.54	24.52	68.51	Trevoy (123)
Benzene-$nC_{18}H_{38}$	3	53.12	32.03	79.61	Trevoy (123)
$nC_{16}H_{34}$-$nC_{14}H_{30}$	11	4.14	3.18	87.57	Heric (47)

Table 4.18 (Continued)

Mixture	No. of Points	AAD %†			Reference
		Method A*	Method C	Dean & Stiel	
nC_7H_{16}-$nC_{14}H_{30}$	3	11.15	20.90	66.50	Trevoy (123)
nC_7H_{16}-$nC_{16}H_{34}$	3	23.32	19.00	73.19	Trevoy (123)
nC_7H_{16}-$nC_{18}H_{38}$	3	29.57	25.70	77.68	Trevoy (123)
nC_7H_{16}-$nC_{12}H_{26}$	6	34.60	73.44	50.71	Trevoy (123)
iC_7H_{16}-$nC_{12}H_{26}$	3	14.76	50.25	51.72	Trevoy (123)
iC_7H_{16}-$nC_{16}H_{34}$	3	31.48	7.86	73.43	Trevoy (123)
Benzene-iC_7H_{16}	3	6.03	1.49	32.24	Trevoy (123)
Benzene-nC_7H_{16}	3	3.81	12.19	31.49	Trevoy (123)
Benzene-$nC_{10}H_{22}$	3	14.00	17.22	49.28	Trevoy (123)
Benzene-nC_6H_{14}	10	5.93	6.03	38.24	Heric (47)
CCl_4-nC_6H_{14}	8	14.76	13.37	43.29	Heric (47)
Benzene-CCl_4	9	28.35	27.52	55.49	Heric (47)
Toluene-nC_8H_{18}	28	14.47	15.06	31.60	Ling (73)
Overall	1585	9.19	7.22	16.20	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

constituents have dissimilar molecular size. This model works well for mixture constituents have molecular weights as large as that of n-decane which correspond very well to compounds found in natural gas. Thus, this model is recommended to predict the viscosity of natural gas or liquified natural gas and also of mixtures of that type. Both methods A and C produce almost similar results when the molecular weight of one of the mixture constituents is greater than that of n-decane. Thus, the conformal solution theory models are recommended for this kind of mixture due to their simplicity and lower calculation time requirements.

For comparison, Wilke's method of equation (2.1.7) was used to predict the viscosity of dilute gas mixtures and the results are presented in Tables 4.14 through 4.17 along with the results produced by this work. Both this work and Wilke's method predicted viscosity with comparable accuracy. Wilke's method did not produce acceptable results for dense nonpolar gas mixtures, therefore; the Dean and Stiel method of equation (2.1.32) was used to calculate the viscosity of dense gas and liquid mixtures. The results are presented in Table 4.18 along with results produced by this work. For similar molecular size mixture constituents, both this work and the Dean and Stiel method produced comparable results for dense gas mixtures but the accuracy of the Dean and Stiel

method gets worse for mixtures with large dissimilar molecular size, such as methane + n-nonane. Also, the Dean and Stiel method does not work well for liquid mixtures. The models presented by this research, generally produced more accurate results than the Dean and Stiel equation.

The superiority of the models presented for viscosity in this work to any other correlation stems from the fact that there is no single correlation in the literature that is capable of predicting the viscosity in all fluid states and for all classes of fluid mixtures, as was discussed in Chapter II. A designer will only have a single correlation to work with instead of working with several of them at the same time. These facts in addition to accuracy makes this correlation the most attractive available.

Of course there is room for improvement in this work. An example is simultaneous regression on both transport and thermodynamic properties to abstract unique values for the binary interaction parameters. Also, the problem of dimerization in the associated fluid mixtures should be looked at carefully. Finally, an equation of state is badly needed to improve the prediction of density which is the main factor in improving dense gas and liquid mixture viscosity predictions.

CHAPTER V

THERMAL CONDUCTIVITY

RESULTS AND DISCUSSION

The same objectives were followed for thermal conductivity as for viscosity. Those objectives were to predict the thermal conductivity by setting the binary interaction parameters in the combing rules of equations (3.2.14) and (3.2.15) equal to unity ($\xi_{ij}=\zeta_{ij}=1.0$), objective I. If the deviations were not within the acceptable limit, then values of the BIPs were obtained from thermodynamics, if available, and inserted in equations (3.2.14) and (3.2.15), objective II. Finally, if thermodynamics does not provide such values, then those values of the BIPs were determined by regression on the experimental transport data, objective III.

Equation (3.5.1) was used to predict the thermal conductivity of several binary mixtures ranging from dilute gas to dense gas and liquid mixtures. The mixture systems were divided into several classes, the various binaries of nonpolar, polar and associating components. A total of 1,393 thermal conductivity points were predicted and compared to experimental data. The experimental thermal conductivity data are summarized in Table 5.1. Two sets of mixing rules are used to calculate the characteristic parameters, σ_x, ε_x, ω_x, μ_x, κ_x and m_x^* for the hypothetical pure fluid representing

Table 5.1 Experimental Thermal Conductivity Data Ranges And References

Mixture	No. of Points	Temp. Range, ^{o}R	Press. Range, Psia	Composition	Reference
Ar-Xe	11	524	13.54	0.00-1.00	Thornton (119)
Ar-Xe	10	544-1,428	14.696	0.00-1.00	Mason (78)
Ar-Xe	8	560	14.696	0.00-1.00	Saxena (103)
Ar-Xe	12	563- 659	14.696	0.00-1.00	Tondon (121)
Ar-Kr	10	524	13.54	0.00-1.00	Thornton (120)
Ar-Kr	10	544-1,428	14.696	0.00-1.00	Mason (78)
Ar-Kr	20	544- 653	14.696	0.00-1.00	Gamhir (35)
Ar-Kr	78	540-2,700	14.696	0.00-1.00	Kestin (64)
Ar-Kr	8	560	14.696	0.00-1.00	Srivastava (111)
Xe-Kr	11	524	13.54	0.00-1.00	Thornton (119)
Xe-Kr	14	544-1,428	14.696	0.00-1.00	Mason (78)
Xe-Kr	18	563- 654	14.696	0.00-1.00	Mathur (79)
CH_4-C_3H_8	32	581- 761	14.696	0.00-1.00	Smith (107)
CH_4-C_3H_8	5	659- 671	14.696	0.00-1.00	Chueng (18)
CH_4-C_2H_4	3	1,062	14.696	0.00-1.00	Chueng (18)
CO_2-C_2H_4	3	1,064	14.696	0.00-1.00	Chueng (18)
CO_2-C_3H_8	5	622- 671	14.696	0.00-1.00	Chueng (18)
CH_4-nC_4H_{10}	53	499- 799	14.696-5,000	0.394	Carmicheal (13)
Benzene-P-Xylene	12	536- 572	14.696	0.00-1.00	Ogiwara (92)
Benzene-nC_7H_{16}	12	536- 572	14.696	0.00-1.00	Ogiwara (92)
nC_7H_{16}-$nC_{10}H_{22}$	10	537- 582	14.696	0.00-1.00	Ogiwara (92)
CH_4-CO_2	20	448- 490	38-1,483	0.5061-1.00	Christensen (17)

Table 5.1 (Continued)

Mixture	No. of Points	Temp. Range, ^{o}R	Press. Range, Psia	Composition	Reference
CH_4-N_2	11	398- 489	42.6-1,262	0.5102	Christensen (17)
O_2N_2	34	541	130-5,248	0.2116	Fleeter (34)
Toluene-O-Xylene	8	491.67	14.696	0.00-1.00	Parkinson (93)
nC_7H_{16}-CCl_4	8	491.67	14.696	0.00-1.00	Parkinson (93)
Toluene-CCl_4	8	491.67	14.696	0.00-1.00	Parkinson (93)
nC_7H_{16}-Cyclopentane	8	491.67	14.696	0.00-1.00	Parkinson (93)
nC_7H_{16}-nC_6H_{14}	8	491.67	14.696	0.00-1.00	Parkinson (93)
nC_7H_{16}-nC_8H_{18}	8	491.67	14.696	0.00-1.00	Parkinson (93)
nC_7H_{16}-Toluene	8	491.67	14.696	0.00-1.00	Parkinson (93)
nC_6H_{14}-nC_8H_{18}	8	491.67	14.696	0.00-1.00	Parkinson (93)
Benzene-Toluene	18	491- 608	14.696	0.00-1.00	Jamieson (56)
Ar-NH_3	22	581- 671	14.696	0.00-1.00	Maczek (77)
CH_4-NH_3	22	581- 671	14.696	0.00-1.00	Maczek (77)
N_2O-NH_3	22	581- 671	14.696	0.00-1.00	Maczek (77)
Ar-SO_2	22	581- 671	14.696	0.00-1.00	Maczek (77)
CH_4-SO_2	22	581- 671	14.696	0.00-1.00	Maczek (77)
N_2O-SO_2	22	581- 671	14.696	0.00-1.00	Maczek (77)
CO_2-SO_2	22	581- 671	14.696	0.00-1.00	Maczek (77)
CCl_4-Chloroform	7	518.67	14.696	0.00-1.00	Filippov (29)
CCl_4-Dichloromethane	7	491.67	14.696	0.00-1.00	Jamieson (55)
$(CH_3)_2O$-CH_3Cl	22	581- 671	14.696	0.00-1.00	Maczek (76)
$(CH_3)_2O$-SO_2	22	581. 671	14.696	0.00-1.00	Maczek (76)

Table 5.1 (Continued)

Mixture	No. of Points	Temp. Range, ^{o}R	Press. Range, Psia	Composition	Reference
CH_3Cl-SO_2	22	581- 671	14.696	0.00-1.00	Maczek (76)
Chloroform-Diethyl Ether	12	401- 491	14.696	0.00-1.00	Jamieson (56)
Dichloromethane-Diethyl Ether	15	401- 491	14.696	0.00-1.00	Jamieson (56)
Methanol-Water	35	527- 635	14.696	0.00-1.00	Filippov (33)
Methanol-Water	9	527- 599	14.696	0.158-0.628	Sobr (109)
Ethanol-Water	51	383- 599	14.696	0.00-1.00	Tsederberg (124)
Ethanol-Water	5	499	14.696	0.00-1.00	Gillam (38)
Ethanol-Water	37	527- 635	14.696	0.00-1.00	Filippov (32)
Ethanol-Water	9	527- 599	14.696	0.115-0.540	Sobr (109)
Ethanol-Water	30	491- 635	14.696	0.00-0.891	Popov (95)
Ethanol-Water	74	527- 635	14.696	0.00-1.00	Riedel (100)
n-Propanol-Water	65	419- 635	14.696	0.00-1.00	Riedel (101)
n-Propanol-Water	9	527- 599	14.696	0.091-0.474	Sobr (110)
Acetone-Water	51	419- 599	14.696	0.00-1.00	Riedel (99)
Toluene-Phenol	21	545- 635	14.696	0.00-1.00	Geller (36)
Chloroform-Methylethyl Ketone	6	546	14.696	0.00-1.00	Kerr (61)
Toluene-Methyl Ethyl Ketone	5	563	14.696	0.00-1.00	Geller (37)
Toluene-Methanol	14	491- 581	14.696	0.00-1.00	Jamieson (56)

Table 5.1 (Continued)

Mixture	No. of Points	Temp. Range, ^{o}R	Press. Range, Psia	Composition	Reference
Aniline-n-Heptanol	15	491- 761	14.696	0.00-1.00	Jamieson (56)
Acetone-Methyl Ethyl Ketone	8	491.67	14.696	0.00-1.00	Parkinson (93)
Methanol-n-Hexanol	18	538- 612	14.696	0.00-1.00	Mukhamedzyanov (90)
CCl_4-n-Heptanol	20	491- 608	14.696	0.00-1.00	Jamieson (56)
CCl_4-i-Butanol	20	491- 608	14.696	0.00-1.00	Jamieson (56)
CCl_4-i-Butanol	8	581.67	14.696	0.00-1.00	Filippov (30)
CCl_4-Methanol	6	581.67	14.696	0.00-1.00	Filippov (31)
CCl_4-Methanol	19	491- 581	14.696	0.00-1.00	Jamieson (56)
CCl_4-Methanol	6	557	14.696	0.00-1.00	Barnette (4)
CCl_4-n-Propanol	6	557	14.696	0.00-1.00	Barnette (5)
CCl_4-Ethanol	6	557	14.696	0.00-1.00	Barnette (3)
CCl_4-n-Butanol	20	491- 608	14.696	0.00-1.00	Jamieson (56)
CCl_4-Sec-Propanol	17	491- 581	14.696	0.00-1.00	Jamieson (56)
CCl_4-Sec-Butanol	15	491- 608	14.696	0.00-1.00	Jamieson (56)
CCl_4-n-Pentanol	11	491- 581	14.696	0.00-1.00	Jamieson (56)
Cyclohexane-n-Propanol	6	557	14.696	0.00-1.00	Barnette (6)
Cyclohexane-Ethanol	6	557	14.696	0.00-1.00	Barnette (7)
$nC_{10}H_{22}$-n-Butanol	12	538- 684	14.696	0.00-1.00	Mekhamedzyanov (89)

Table 5.2: Summary of Thermal Conductivity Results For Dilute Nonpolar Gas Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
Ar-Xe	11	0.99	0.84	Thornton (119)
Ar-Xe	10	5.39	4.50	Mason (78)
Ar-Xe	8	1.60	2.53	Saxena (103)
Ar-Xe	12	4.00	3.46	Tondon (121)
Ar-Kr	10	4.00	4.86	Thornton (120)
Ar-Kr	10	3.63	3.10	Mason (78)
Ar-Kr	20	1.98	2.70	Gamhir (35)
Ar-Kr	78	1.80	1.58	Kestin (64)
Ar-Kr	8	3.37	4.14	Srivastava (111)
Xe-Kr	11	1.88	1.53	Thornton (119)
Xe-Kr	14	3.54	3.69	Mason (78)
Xe-Kr	18	4.16	4.43	Mathur (79)
CH_4-C_3H_8	32	2.82	2.03	Smith (107)
CH_4-C_3H_8	5	2.98	0.63	Chueng (18)
CH_4-C_2H_4	3	3.26	3.25	Chueng (18)
$CO_2C_2H_4$	3	1.74	1.88	Chueng (18)
CO_2-C_3H_8	5	3.54	1.41	Chueng (18)
Overall	258	2.68	2.50	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100/\text{No. of Points}$

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

the mixture. Those rules are summarized in Table 3.2.1 as the modified van der Waals one fluid mixing rules, set A and the semiempirical exponent mixing rules, set B, which will be referred and in the subsequent discussion as methods A and B respectively.

Table 5.2 presents the results of the thermal conductivity predictions for several dilute nonpolar gas mixtures. A total of 258 binary points were predicted and compared to experimental values. All the calculations were performed with unity values for the BIPs. In this case, as was for the same viscosity case, the use of unity BIPs proved to be adequate. The percentage average absolute deviations were 2.68% and 2.50% for methods A and B, respectively. These results lead to the conclusion that no binary interactions parameters are needed to predict the thermal conductivity of dilute nonpolar gas mixtures. The reason for this behavior is attributed to the same reason given for the dilute viscosity case. The thermal conductivity is a strong function of the kinetic energy in the dilute case and a function of temperature only. Density does not make a contribution in the dilute gas state. The density contibution does not become apparent until the gas mixture is more compressed or is in the liquid state. This means any correction to σ_{ij} will not have any effect in the dilute gaseous state.

Results for dilute nonpolar-polar gas mixtures are presented in Table 5.3. The thermal conductivity for 154 binary points were predicted and compared to experimenal data and the AAD were 4.64% and 3.96% for methods A and B, respectively. These calculations were performed with unity BIPs. The same conclusions as for the dilute nonpolar gas case applies here.

Dilute polar gas mixtures results are presented in Table 5.4 where the thermal conductivity for 66 binary points were predicted and compared to experimental data. As was done previously, the BIPs are fixed at unity values. The AAD were 3.10% for both methods A and B. The same conclusions are applicable in this case as in the other dilute gas mixture classes.

No experimental data were found to test dilute associated gas mixtures but if the dilute gas viscosity trends for other gases are followed the thermal conductivity of any dilute gas mixture can be predicted reasonably accurately.

It is clear from the previous discussion that application of either the modified van der Waals one fluid mixing rules, method A, or the semiempirical exponent mixing rules, method B, will produce comparable results. Method A gave an AAD of 3.37% for all of the dilute gas mixtures (478 points) while method B gave an AAD of 3.05%. These results meet the

Table 5.3 Summary of Thermal Conductivity Results of Dilute Nonpolar-Polar Gas Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
$Ar-NH_3$	22	5.14	5.62	Maczek (77)
CH_4-NH_3	22	3.59	1.86	Maczek (77)
N_2O-NH_3	22	4.10	2.63	Maczek (77)
$Ar-SO_2$	22	0.62	2.79	Maczek (77)
CH_4-SO_2	22	9.06	4.51	Maczek (77)
N_2O-SO_2	22	5.52	5.74	Maczek (77)
CO_2-SO_2	22	4.46	4.94	Maczek (77)
Overall	154	4.64	3.96	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 5.4 Summary of Thermal Conductivity Results For Dilute Polar Gas Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
$(CH_3)_2O$-CH_3Cl	22	2.20	2.20	Maczek (76)
$(CH_3)_2O$-SO_2	22	5.49	5.49	Maczek (76)
CH_3Cl-SO_2	22	1.63	1.63	Maczek (76)
Overall	66	3.10	3.10	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 5.5: Summary of Thermal Conductivity Results for Nonpolar Dense Gas And Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
CH_4-nC_4H_{10}	53	5.05	3.90	Carmicheal (13)
Benzene-P-Xylene	12	9.60	10.60	Ogiwora (92)
Benzene-nC_7H_{16}	12	4.66	2.94	Ogiwora (92)
nC_7H_{16}-$nC_{10}H_{22}$	10	1.77	1.63	Ogiwora (92)
CH_4-CO_2	20	13.86	10.86	Christensen (17)
CH_4-N_2	11	6.90	7.22	Christensen (17)
O_2-N_2	34	4.25	4.29	Fleeter (34)
Toluene-O-Xylene	8	4.93	5.04	Parkinson (93)
nC_7H_{16}-CCl_4	8	3.86	5.52	Parkinson (93)
Toluene-CCl_4	8	3.04	3.15	Parkinson (93)
nC_7H_{16}-Cyclopentane	8	3.15	1.58	Parkinson (93)
nC_7H_{16}-nC_6H_{14}	8	1.19	1.26	Parkinson (93)
nC_7H_{16}-nC_8H_{18}	8	3.46	3.54	Parkinson (93)
nC_7H_{16}-Toluene	8	0.94	1.24	Parkinson (93)
nC_6H_{14}-nC_8H_{18}	8	3.09	3.09	Parkinson (93)
Benzene-Toluene	18	3.01	2.09	Jamieson (106)
Overall	234	4.73	4.60	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters taken to be unity ($\xi = \zeta = 1.0$)

Table 5.6 Summary of Thermal Conductivity Results For Nonpolar-Polar Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
CCl_4-Chloroform	7	5.72	5.56	Filippov (29)
CCl_4-Dichloromethane	7	10.49	9.47	Jamieson (55)
Overall	14	8.11	7.52	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

requirements of objective I, which is the prediction of thermal conductivity with unity binary interaction parameters.

Results for nonpolar dense gas and liquid mixtures are presented in Table 5.5. For this class of mixtures, a total of 234 binary mixture points were predicted and compared with experimental data. Predictions with unity BIPs are reported in Table 5.5 because it was found that in almost all the systems tested good results were obtained by this approach, i.e., there was not need to use values for the BIPs other than unity. One reason for this is that all systems tested are of similar molecular size constituents because no experimental data were available in the literature for systems with greatly dissimilar molecular sizes (such as methane + n-decane mixture). It is possible that such a system might require the use of the BIPs but this cannot be discussed until such experimental data are available. The AAD obtained for the nonpolar dense gas and liquid mixtures are 4.73% for method A and 4.60% for method B.

Experimental data are scarce for nonpolar-polar dense gas and liquid mixtures and only two mixture systems (14 points) were found in this class. Table 5.6 presents the results for these systems. In general, it was found that unity BIPs produced satisfactory results. AAD's of 8.11% for method A and 7.52% for method B were obtained. More experimental data would be required to draw meaningful

Table 5.7 Summary of Thermal Conductivity Results For Polar Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A*	Method B*	
Chloroform-Diethyleter	12	4.47	4.71	Jamieson (56)
Dichloromethane-Diethylether	15	11.52	10.62	Jamieson (56)
Overall	27	8.38	8.00	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100] /$ No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \varsigma = 1.0$)

conclusions.

As was the case for nonpolar-polar dense gas and liquid mixtures, polar dense gas and liquid mixtures lack experimental data and only two mixture systems (27 points) were obtained from the literature. Method A produced an AAD of 8.38% and method B produced an AAD of 8.00%. Again, no solid conclusions can be drawn until more experimental data are available.

Results for liquid mixtures with association effects are divided into three parts. The first part which is summarized in Table 5.8 represents associated-associated mixtures. Column I of this table presents the results obtained with unity values for the binary interaction parameters (BIPs). The average absolute deviation for this case is 23.39% by method A and 28.35% by method B for 416 binary points. A few mixture system thermal conductivity values are predicted with reasonable accuracy, but for most of the systems deviations are quite high. These results indicate that binary interaction parameters are needed to improve the accuracy of prediction. As mentioned previously in the viscosity case, thermodynamics presently does not provide the BIP values for such systems because of the lack of an equation of state that can predict the thermodynamic properties of associated fluids. Thus, the binary interaction parameters were determined by regression on the experimental thermal conductivity data. As was concluded from the dilute gas mixtures case, the energy parameter ε_{ij} does not need any correction which means the binary interaction parameter, ζ_{ij}, corresponding to ε_{ij} can be

Table 5.8 Summary of Thermal Conductivity Results For Associated-Associated Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Methanol-Water	35	39.58	--	17.83	50.09	--	21.92	Filippov (33)
Methanol-Water	9	25.75	--	9.37	40.50	--	9.41	Sobr (109)
Ethanol-Water	51	19.08	--	10.37	28.11	--	13.03	Tsederberg (124)
Ethanol-Water	5	41.82	--	11.67	46.88	--	10.42	Gillam (38)
Ethanol-Water	37	37.47	--	20.44	43.54	--	24.68	Filippov (32)
Ethanol-Water	9	18.37	--	9.83	23.55	--	12.54	Sobr (109)
Ethanol-Water	30	18.48	--	10.16	22.18	--	12.27	Popov (95)
Ethanol-Water	74	20.32	--	9.78	26.26	--	11.44	Riedel (100)
n-Propahol-Water	65	21.94	--	9.21	23.08	--	10.85	Riedel (101)
n-Propanol-Water	9	18.17	--	4.56	21.75	--	7.33	Sobr (110)
Acetone-Water	51	22.03	--	9.64	25.85	--	10.18	Riedel (99)
Aniline-n-Heptanol	15	10.07	--	--	9.83	--	--	Jamieson (56)
Acetone-Methyl Ethyl Ketone	8	35.45	--	19.47	37.80	--	19.19	Parkinson(93)
Methanol-n-Hexanol	18	9.53	--	--	6.29	--	--	Mukhamedzyanov (90)
Overall	416	23.39	--	--	28.35	--	--	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

**Binary interaction parameters are obtained from thermodynamics

***Binary interaction parameters are obtained from experimental transport data

taken as unity. The only parameter to be determined will then be ξ_{ij} which is related to the separation parameter σ_{ij}. In the liquid phase the thermal conductivity is very sensitive to the density, which is directly related to σ_{ij}. Results obtained by using this approach, are presented in column III of Table 5.8. The improvement over results obtained using unity BIPs is quite clear and supports the approach previously discussed. As an example for the system ethanol-water, six mixtures from different sources were available and only two of them were used to determine the binary interaction parameter ξ_{ij} for σ_{ij} while keeping $\zeta_{ij} = 1.0$. The values of ξ_{ij}, when used for the other four systems, improved the accuracy in each one of them. This indicates that the BIPs determined this way can be used for practical thermal conductivity predictions. Although, the accuracy of prediction improved drastically with the use of one binary interaction parameter, the deviation is still high compared to the nonassociated fluid mixtures. The reason for the still high deviations is not clear but one of the reasons might lie in the fact that effectively, dimerization can take place between the mixture constituents due to the strong hydrogen bonding between them. This will create a new single compound with completely different values for the association parameter , κ_x, which cannot be predicted by the simple mixing rule. This phenomena demands more studies and may require a completely different approach from conformal

solution theory.

Table 5.9 presents the results for the second group of the associated mixtures which are nonpolar-associated. As was done before, Column I presents those results obtained using unity BIPs with AAD's of 19.50% and 18.35% for methods A and B respectively for a total of 178 binary points. Column III of the same table presents those results when the binary interaction parameter ξ_{ij} was determined from experimental data while ζ_{ij} was kept at unity value. Improvement is quite noticeable when the binary interaction parameter was used over those results with unity values. The same conclusions drawn for the associated-associated liquid mixtures apply also for the associated nonpolar-polar liquid mixtures.

Finally, Table 5.10 presents the results for the third group of the associated mixtures which are polar-associated. With unity BIPs, method A produced an AAD of 10.12% and method B produced 10.36% for 46 thermal conductivity points. The conclusions remain the same as for the previously discussed associated mixtures.

The value of the unlike parameter κ_{ij} used for the thermal conductivity predictions presented in Table 5.8 through 5.10 was calculated by equation (3.2.16). This equation did not predict a good value for κ_{ij} of liquid mixtures, thus equations (3.2.18a) and (3.2.18b) are used along with the generalized binary interaction parameters of equations (3.2.19) and 3.2.20) for ξ_{ij} and ϕ_{ij}. The results

Table 5.9 Summary of Thermal Conductivity Results For Nonpolar-Associated Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %[+]						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
CCl_4-n-Heptanol	20	7.65	--	--	8.12	--	--	Jamieson (56)
CCl_4-i-Butanol	20	24.66	--	13.06	24.83	--	13.16	Jamieson (56)
CCl_4-i-Butanol	8	27.01	--	15.33	27.19	--	15.41	Filippov (30)
CCl_4-Methanol	6	9.98	--	--	14.47	--	--	Filippov (31)
CCl_4-Methanol	19	9.21	--	--	12.39	--	--	Jamieson (56)
CCl_4-Methanol	6	7.47	--	--	10.71	--	--	Barnette (4)
CCl_4-n-Propanol	6	14.30	--	--	14.87	--	--	Barnette (5)
CCl_4-Ethanol	6	12.78	--	--	14.92	--	--	Barnette (3)
CCl_4-n-Butanol	20	38.41	--	28.76	38.31	--	28.58	Jamieson (56)
CCl_4-Sec-Propanol	17	26.93	--	13.00	28.63	--	13.18	Jamieson (56)
CCl_4-Sec-Butanol	15	19.27	--	8.55	19.70	--	8.66	Jamieson (56)
CCl_4-n-Pentanol	11	18.11	--	8.49	17.94	--	8.76	Jamieson (56)
Cyclohexane-n-Propanol	6	17.01	--	7.72	17.90	--	7.48	Barnette (6)
Cyclohexane-Ethanol	6	10.44	--	--	13.10	--	--	Barnette (7)
n-$C_{10}H_{22}$-n-Butanol	12	6.90	--	--	8.13	--	--	Mukhamedzyanov (89)
Overall	178	19.50	--	--	18.35	--	--	

[+] Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

* Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

* Binary interaction parameters are obtained from thermodynamics

* Binary interaction parameters are obtained from experimental transport data

Table 5.10 Summary of Thermal Conductivity Results For Polar-Associated Liquid Mixtures

Mixture	No. of Points	Avg. Abs. Dev. %†						Reference
		Method A			Method B			
		I*	II**	III***	I*	II**	III***	
Toluene-Phenol	21	6.41	--	--	5.54	--	--	Geller (36)
Cholorform-Methyl Ethyl Ketone	6	18.77	--	12.40	18.65	--	12.75	Kerr (61)
Toluene-Methanol	14	7.36	--	--	9.59	--	--	Jamieson (56)
Toluene-Methyl Propyl Ketone	5	23.03	--	17.28	22.81	--	17.17	Geller (37)
Overall	46	10.12	--	--	10.36	--	--	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

**Binary interaction parameters are obtained from thermodynamics

***Binary interaction parameters are obtained from experimental transport data

of this approach are presented in Table 5.11 for binary associated-associated liquid mixtures, Table 5.12 for binary nonpolar-associated liquid mixtures and Table 5.13 for polar-associated liquid mixtures. This approach predicted thermal conductivies with AAD of 14.66%, 12.79% and 13.46% by method A, respectively and 15.15%, 12.43% and 12.01% by method B, respectively. This approach clearly reduced the average absolute deviations for all mixtures containing associated compound, but the effect is greatest for associated-associated mixtures, for which an AAD of 14.66% produced by this approach compared to 23.39% produced by method A, as previously discussed. The use of equations (3.2.18a) and (3.2.18b) is recommended over equation (3.2.16) for liquid mixtures containing associated compounds. Equation (3.2.16) is still good for dilute gas mixtures containing associated compounds.

For comparison, the Mason and Saxena method of equation (2.2.5) was used to predict the thermal conductivity of dilute gas mixtures and the results are presented in Tables 4.14 through 4.16 along with the results produced by this work. Both this work and the Mason and Saxena method predicted thermal conductivity with comparable accuracy. The Mason and Saxena method does not work for dense gas and liquid mixtures, therefore; the Stiel and Thodos method of equations (3.2.17) through (3.2.19) was used to calculate the thermal conductivity of dense gas and liquid mixtures. The results are presented in Table 5.17 along with results produced by

Table 5.11: Summary of Thermal Conductivity Results For Associated Liquid Mixtures With The Generalized Binary Interaction Parameters

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A	Method B	
Methanol-Water	35	11.71	17.66	Fillippov (33)
Methanol-Water	9	10.90	10.29	Sobr (109)
Ethanol-Water	51	13.53	12.60	Tsederberg (124)
Ethanol-Water	5	21.29	20.87	Gillam (38)
Ethanol-Water	37	22.04	22.43	Filippov (32)
Ethanol-Water	9	10.57	10.62	Sobr (109)
Ethanol-Water	30	10.69	10.55	Popov (95)
Ethanol-Water	74	12.47	11.68	Riedel (100)
n-Propanol-Water	65	17.82	18.29	Riedil (101)
n-Propanol-Water	9	15.40	16.17	Sobr (110)
Acetone-Water	51	15.33	17.10	Riedel (99)
Aniline-n-Heptanol	15	8.12	9.26	Jamieson (56)
Acetone-Methyl Ethyl Ketone	8	32.67	31.13	Parkinson (93)
Methanol-n-Hexanol	18	9.97	8.09	Mukhamedzyanol (90)
Overall	416	14.66	15.15	

†Avg. Abs. Dev. % = $[\Sigma \frac{\lambda_{exp} - \lambda_{cal}}{\lambda_{exp}} \times 100]$/No. of Points

Table 5.12: Summary of Thermal Conductivity Results For Nonpolar-Associated Liquid Mixtures With The Generalized Binary Interaction Paramters

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A	Method B	
CCl_4-n-Heptanol	20	8.44	6.70	Jamieson (56)
CCl_4-i-Butanol	20	12.43	13.43	Jamieson (56)
CCl_4-i-Butanol	8	14.10	14.42	Filippov (30)
CCl_4-Methanol	6	14.39	10.35	Filippov (31)
CCl_4-Methanol	19	9.61	7.02	Jamieson (56)
CCl_4-Methanol	6	10.74	7.89	Barnette (5)
CCl_4-n-Propanol	6	8.80	8.12	Barnette (5)
CCl_4-Ethanol	6	8.82	7.74	Barnette (3)
CCl_4-n-Butanol	20	33.35	34.11	Jamieson (56)
CCl_4-Sec-Propanol	17	12.85	14.15	Jamieson (56)
CCl_4-Sec-Butanol	15	7.88	8.30	Jamieson (56)
CCl_4-n-Pentanol	11	8.05	9.13	Jamieson (56)
Cyclohexane-n-Propanol	6	10.14	13.05	Barnette (6)
Cyclohexane-Ethanol	6	4.44	5.78	Barnette (7)
$nC_{10}H_{22}$-n-Butanol	12	10.64	8.04	Mukhamedzyanov (89)
Overall	178	12.79	12.43	

†Avg. Abs. Dev. % = $[\Sigma \frac{\lambda_{exp} - \lambda_{cal}}{\lambda_{exp}} \times 100]$/No. of Points

Table 5.13: Summary of Thermal Conductivity Results For Polar-Associated Liquid Mixtures With The Generalized Binary Interaction Parameters

Mixture	No. of Points	Avg. Abs. Dev. %†		Reference
		Method A	Method B	
Toluene-Phenol	21	5.83	7.16	Geller (36)
Chloroform-Methyl-Ethyl Ketone	6	23.30	22.33	Kerr (61)
Toluene-Methanol	14	16.68	10.82	Jamieson (56)
Toluene-Methyl Propyl Ketone	5	24.68	23.31	Geller (37)
Overall	46	13.47	12.01	

†Avg. Abs. Dev. % = $[\Sigma \frac{\lambda_{exp} - \lambda_{cal}}{\lambda_{exp}} \times 100]$/No. of Points

Table 5.14 Comparison Between This Work And The Mason And Saxena's Equation (2.2.5) For The Thermal Conductivity Of Dilute Nonpolar Gas Mixture

Mixture	No. of Points	AAD%†		Reference
		Method A*	Mason & Saxena	
Ar-Xe	11	0.99	5.73	Thornton (119)
Ar-Xe	10	5.39	3.12	Mason (78)
Ar-Xe	8	1.60	7.24	Saxena (103)
Ar-Xe	12	4.00	5.42	Tondon (121)
Ar-Kr	10	4.00	5.85	Thornton (120)
Ar-Kr	10	3.63	2.85	Mason (78)
Ar-Kr	20	1.98	3.49	Gamhir (35)
Ar-Kr	78	1.80	1.71	Kestin (64)
Ar-Kr	8	3.37	5.04	Srivastava (111)
Xe-Kr	11	1.88	2.90	Thornton (119)
Xe-Kr	14	3.54	3.27	Mason (78)
Xe-Kr	18	4.16	3.20	Mathur (79)
CH_4-C_3H_8	32	2.82	1.70	Smith (107)
CH_4-C_3H_8	5	2.98	1.44	Chueng (18)
CH_4-C_2H_4	3	3.26	3.22	Chueng (18)
CO_2-C_2H_4	3	1.74	1.59	Chueng (18)
CO_2-C_3H_8	5	3.54	1.19	Cheung (18)
Overall	258	2.68	3.05	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 5.15 Comparison Between This Work And The Mason And Saxena's Equation (2.2.5) For The Thermal Conductivity of Dilute Nonpolar-Polar Gas Mixtures

Mixture	No. of Points	AAD%†		Reference
		Method A*	Mason & Saxena	
$Ar-NH_3$	22	5.14	1.14	Maczek (77)
CH_4-NH_3	22	3.59	2.41	Maczek (77)
N_2O-NH_3	22	4.10	2.74	Maczek (77)
$Ar-SO_2$	22	0.62	2.60	Maczek (77)
CH_4-SO_2	22	9.06	1.38	Maczek (77)
N_2O-SO_2	22	5.52	3.81	Maczek (77)
CO_2-SO_2	22	4.46	2.92	Maczek (77)
Overall	154	4.64	2.43	

†Avg. Ab. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 5.16 Comparison Between This Work And The Mason And Saxena's Equation (2.2.5) For The Thermal Conductivity of Dilute Polar Gas Mixtures

Mixture	No. of Points	AAD %†		Reference
		Method A*	Mason & Saxena	
$(CH_3)O$-CH_3Cl	22	2.20	2.24	Maczek (76)
$(CH_3)O$-SO_2	22	5.49	2.74	Maczek (76)
CH_3Cl-SO_2	22	1.63	1.53	Maczek (76)
Overall	66	3.10	2.17	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

Table 5.17 Comparison Between This Work And The Stiel And Thodos Equations (2.217) Through (2.2.19) For The Thermal Conductivity of Nonpolar Dense Gas And Liquid Mixtures

Mixture	No. of Points	AAD%†		Reference
		Method A*	Stiel & Thodos	
CH_4-nC_4H_{10}	53	5.05	9.53	Carmicheal (13)
Benzene-P-Xylene	12	9.60	7.45	Ogiwara (92)
Benzene-nC_7H_{16}	12	4.66	19.84	Ogiwara (92)
nC_7H_{16}-$nC_{10}H_{22}$	10	1.77	22.34	Ogiwara (92)
CH_4-CO_2	20	13.86	7.90	Christensen (17)
CH_4-N_2	11	6.90	4.90	Christensen (17)
O_2-N_2	34	4.25	1.24	Fleeter (34)
Toluene-O-Xylene	8	4.93	0.58	Parkinson (93)
nC_7H_{16}-CCl_4	8	3.86	13.15	Parkinson (93)
Toluene-CCl_4	8	3.04	6.30	Parkinson (93)
nC_7H_{16}-Cyclopentane	8	3.15	18.09	Parkinson (93)
nC_7H_{16}-nC_6H_{14}	8	1.19	14.42	Parkinson (93)
nC_7H_{16}-nC_8H_{18}	8	3.46	16.47	Parkinson (93)
nC_7H_{16}-Toluene	8	0.94	7.79	Parkinson (93)
nC_6H_{14}-nC_8H_{18}	8	3.09	14.59	Parkinson (93)
Benzene-Toluene	18	3.01	9.27	Jamieson (56)
Overall	234	4.73	9.44	

†Avg. Abs. Dev. % = $[\Sigma \frac{|\lambda_{exp} - \lambda_{cal}|}{\lambda_{exp}} \times 100]$/No. of Points

*Binary interaction parameters are taken to be unity ($\xi = \zeta = 1.0$)

this work. In general, this work predicted thermal conductivities more accurately than the Stiel and Thodos method, particularly of liquid mixtures.

To summarize the thermal conductivity results, conformal solution theory approach provides the design engineer with an easy way to calculate the thermal conductivity of various classes of mixtures over a wide range of fluid states. The accuracy of prediction is quite satisfactory with unity binary interaction parameters for dilute gas mixtures of all classes and for the dense gas and liquid nonpolar, polar and polar-nonpolar mixtures. BIPs are required for mixtures with association effects. The predicted values are graphically compared with the corresponding experimental values for some selected mixture systems in Figures 5.1 through 5.13.

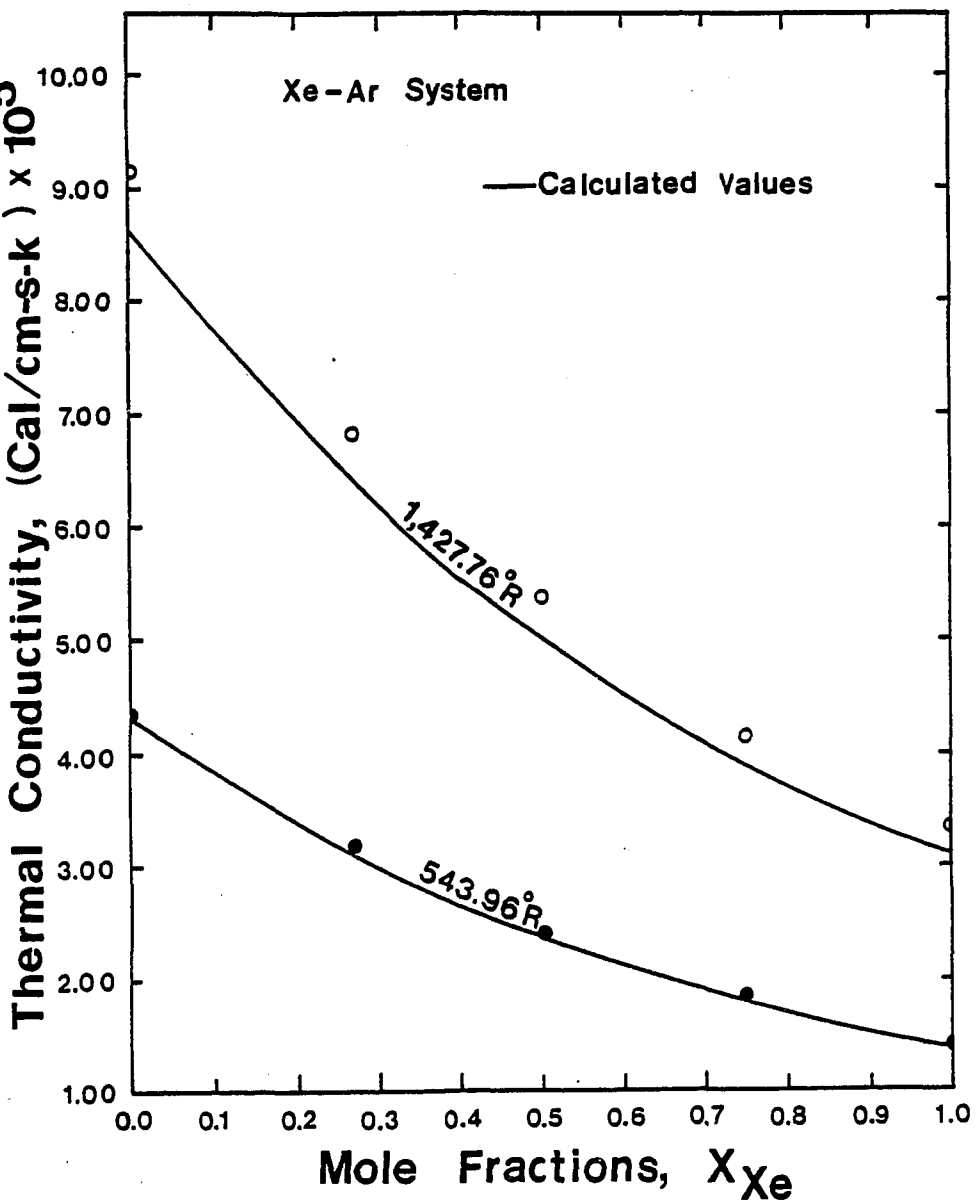

Figure 5.1 Comparison between correlation (Method B) and experimental Xe-Ar dilute gas mixture thermal conductivity data of Mason (78).

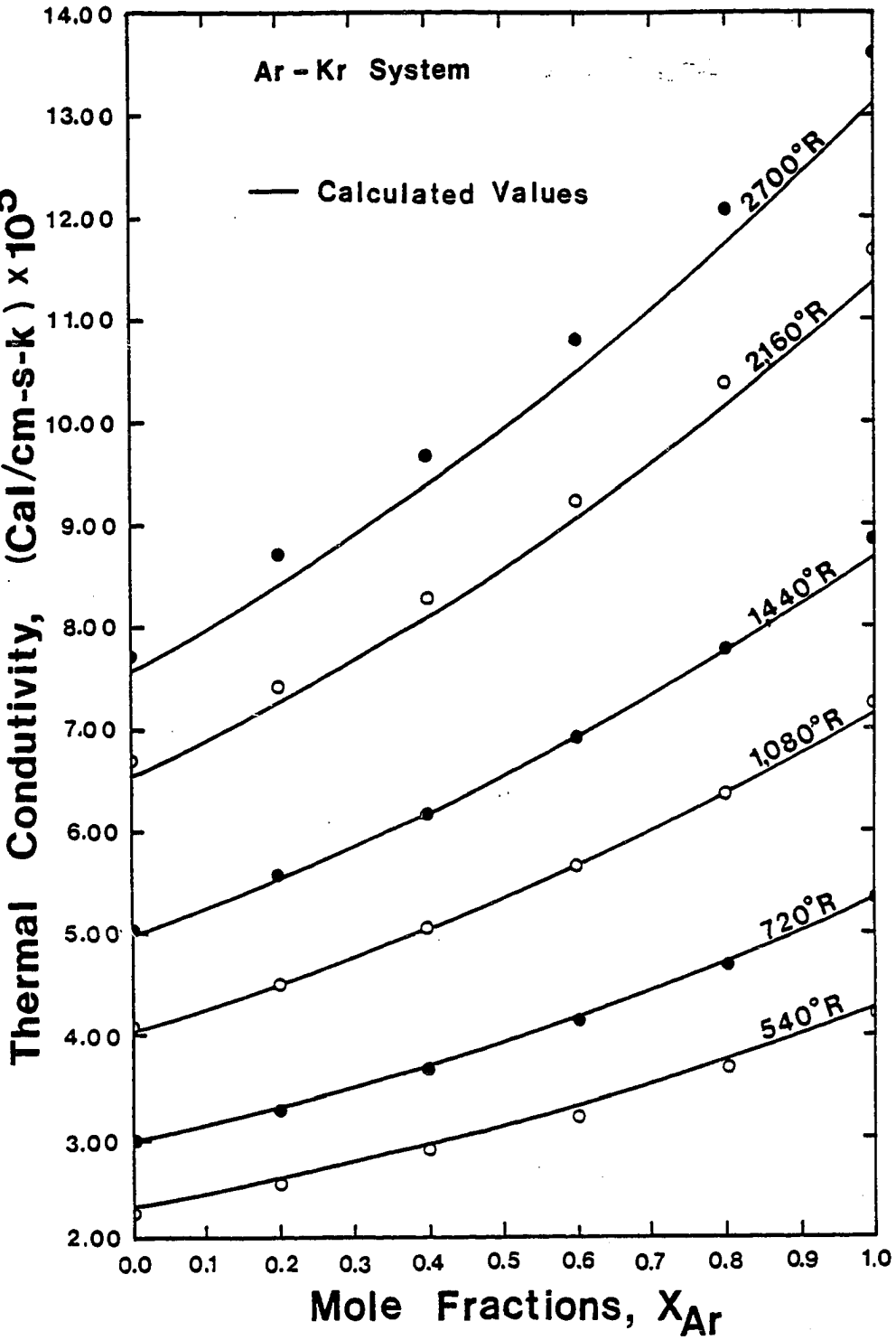

Figure 5.2 Comparison between correlation (Method B) and experimental Ar-Kr dilute gas mixture thermal conductivity data of Kestin (64).

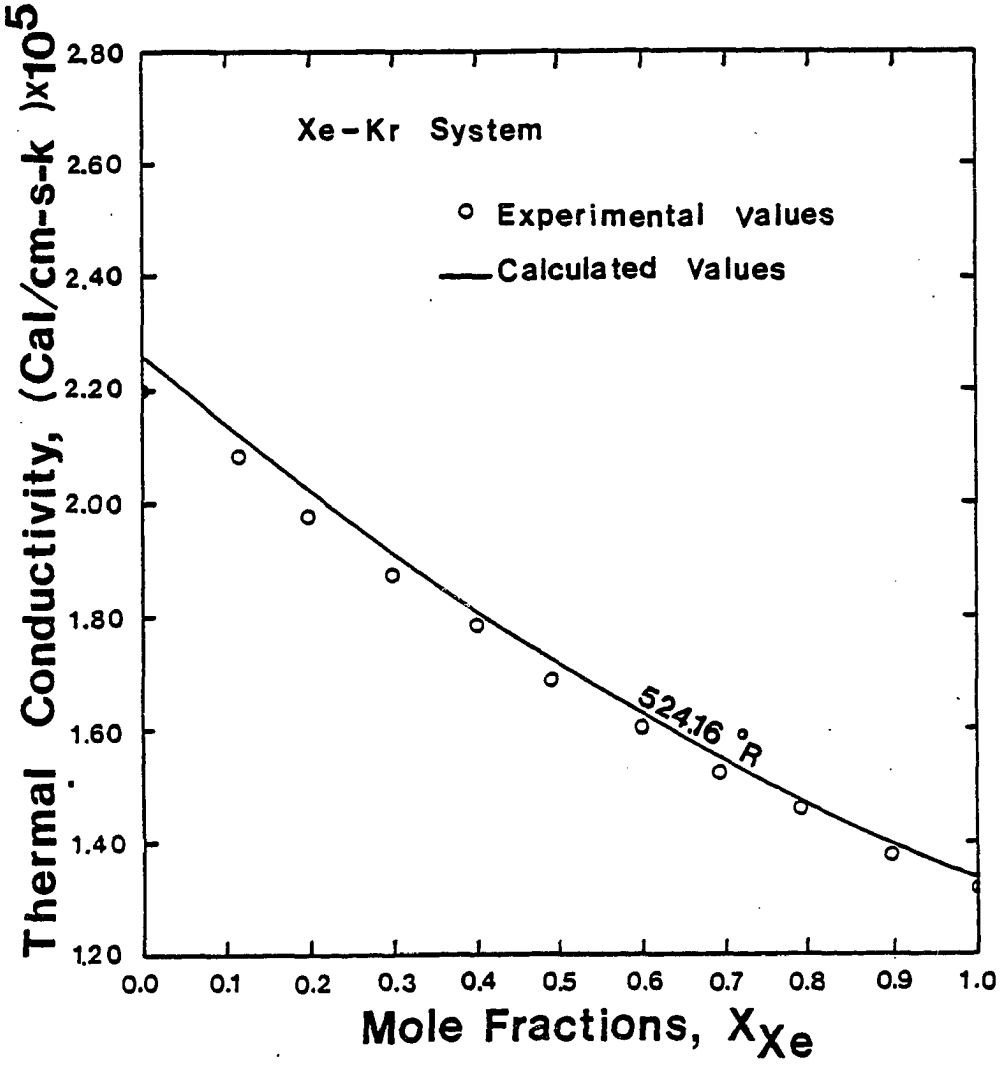

Figure 5.3 Comparison between correlation (Method B) and experimental Xe-Kr dilute gas mixture thermal conductivity data of Thornton (119).

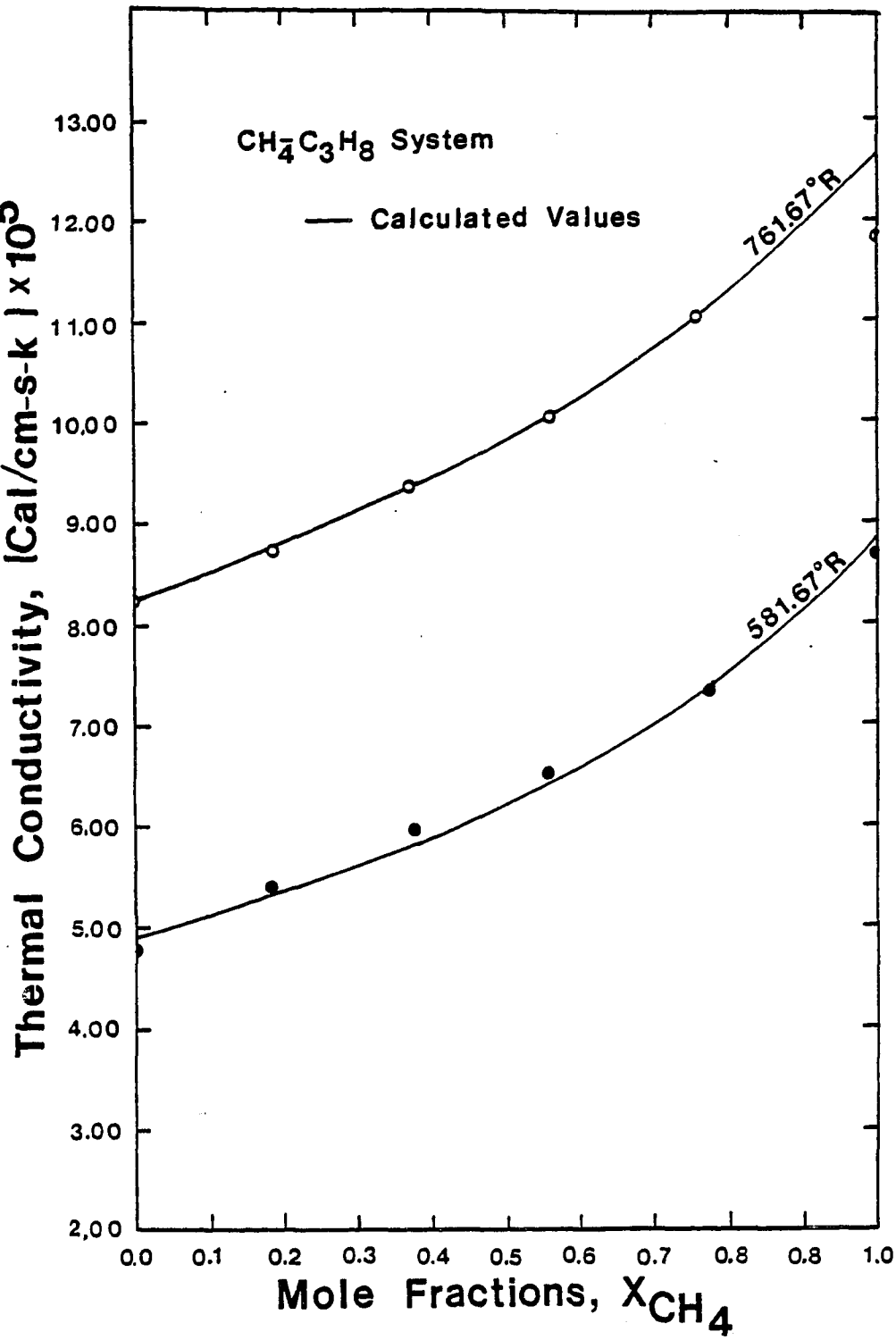

Figure 5.4 Comparison between correlation (Method B) and experimental CH_4-C_3H_8 dilute gas mixture thermal conductivity data of Smith (107).

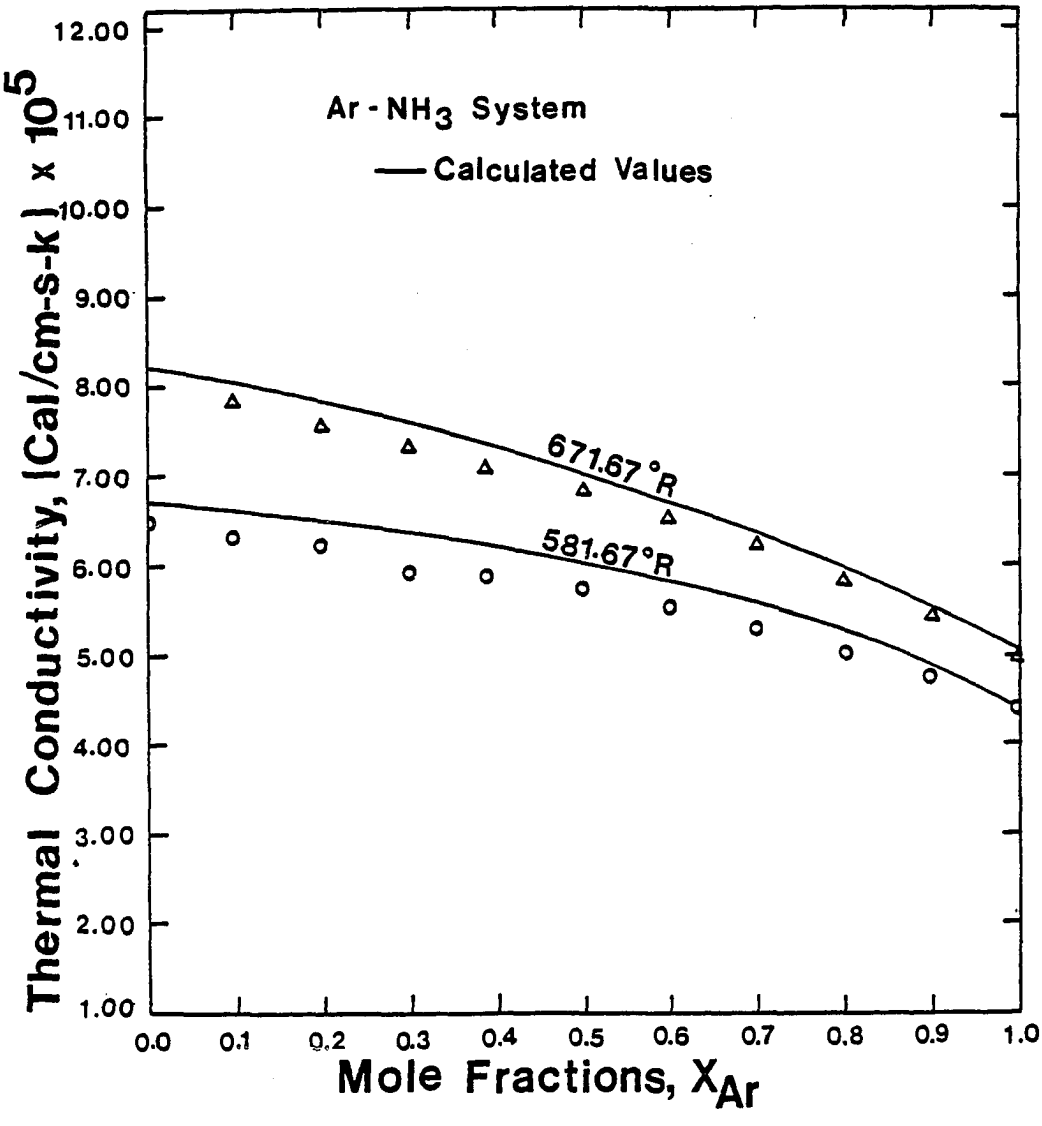

Figure 5.5 Comparison between correlation (Method B) and experimental Ar-NH_3 dilute gas mixture thermal conductivity data of Maczek (77).

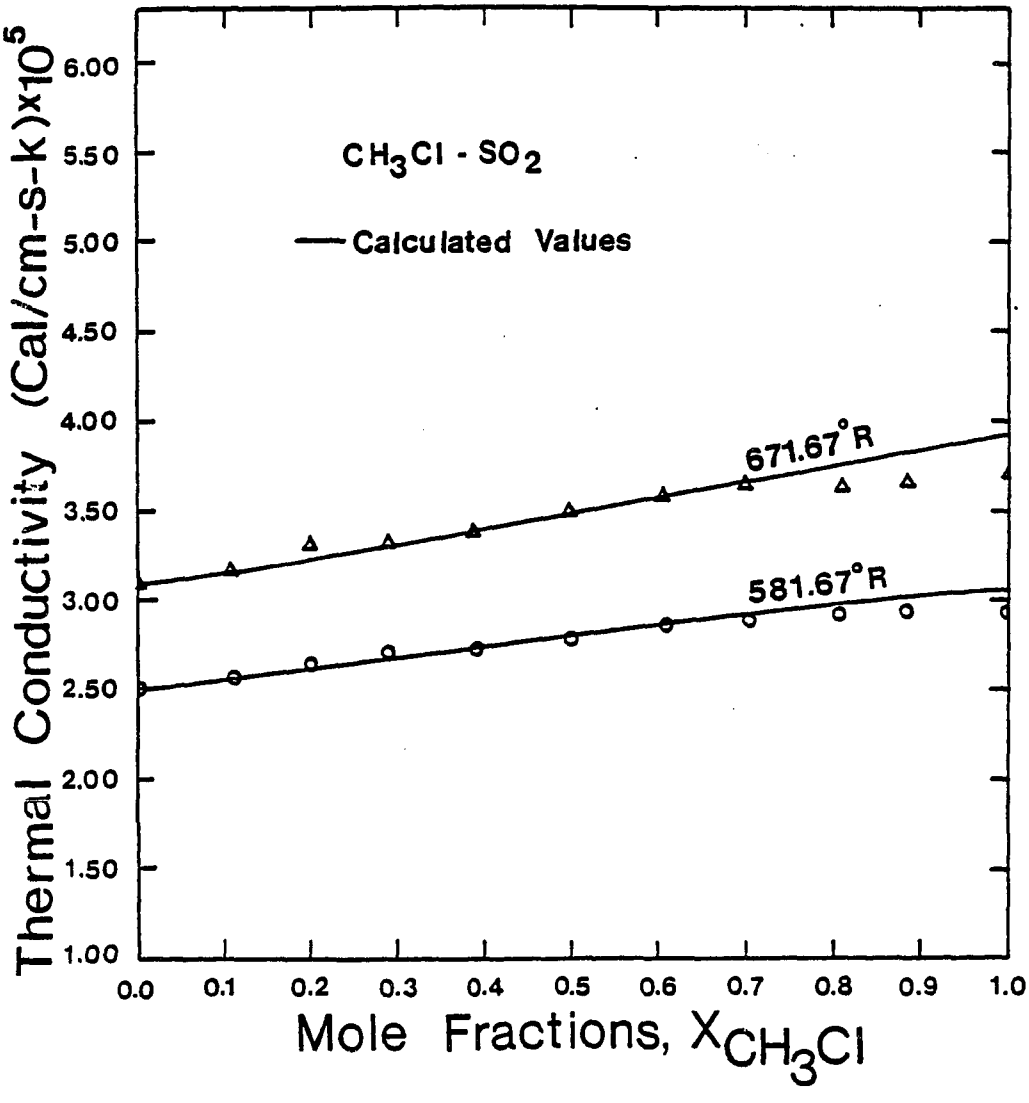

Figure 5.6 Comparison between correlation (Method B) and experimental CH_3Cl-SO_2 dilute gas mixture thermal conductivity data of Macezk (76).

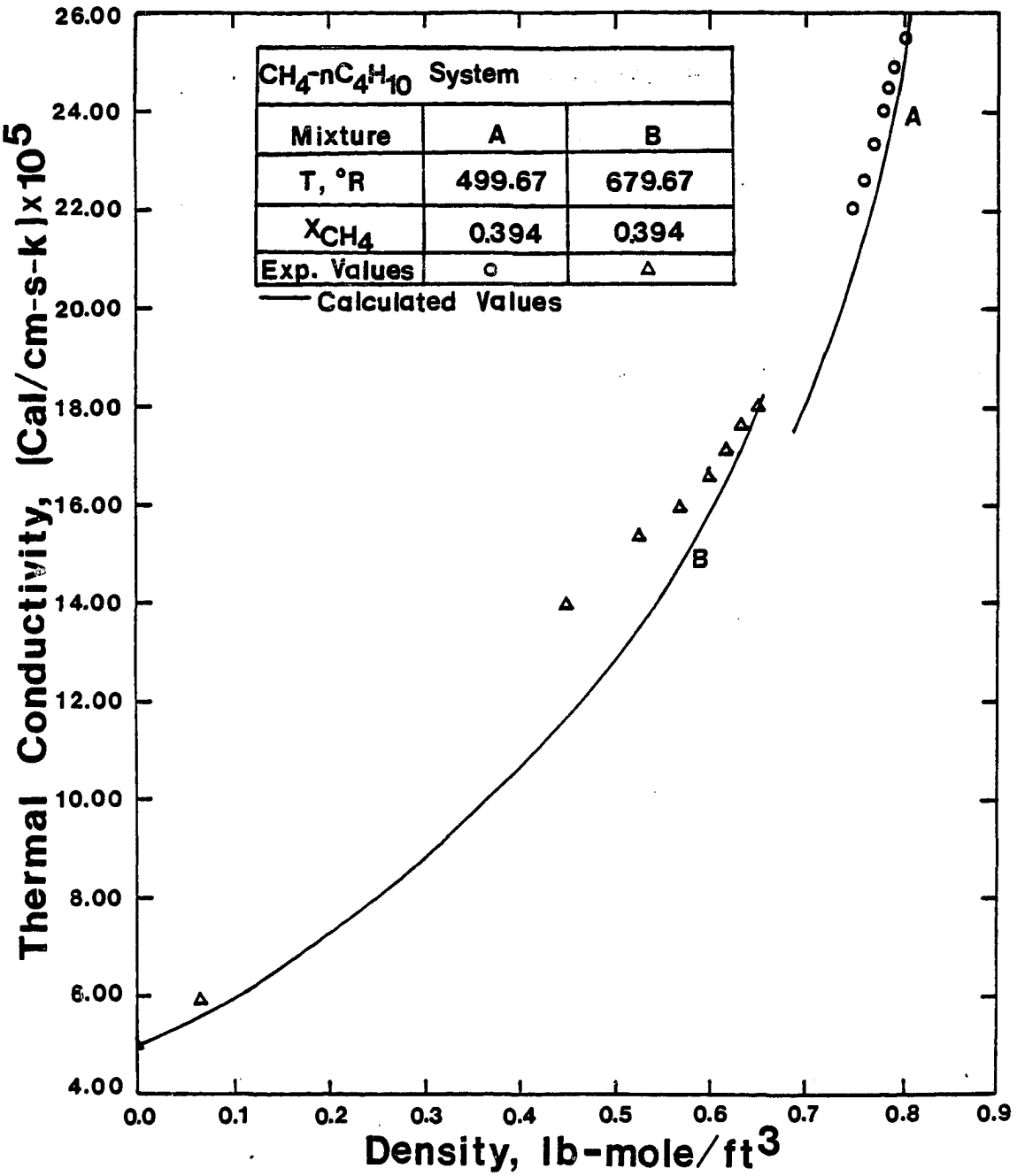

Figure 5.7 Comparison between correlation (Method B) and experimental CH_4-nC_4H_{10} dense gas mixture thermal conductivity data of Carmicheal (13).

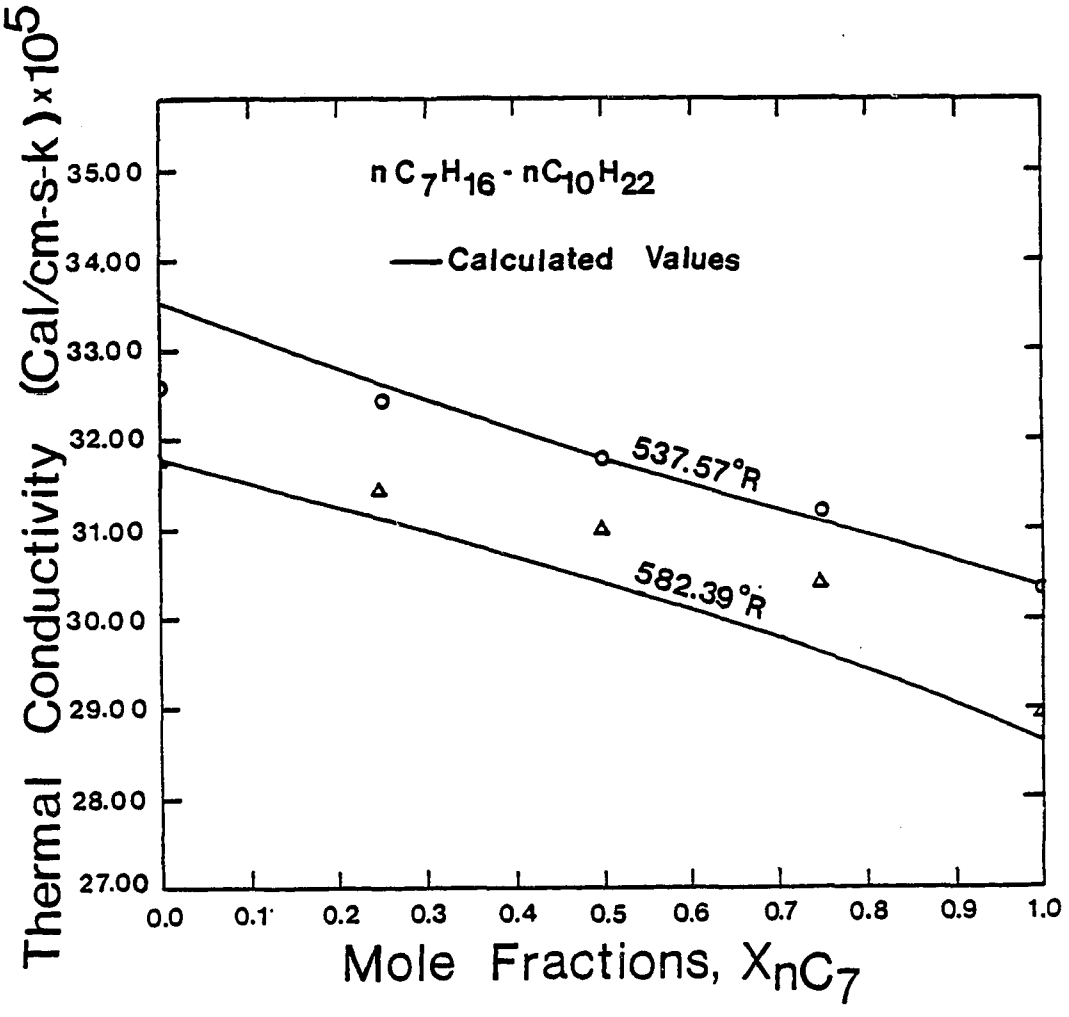

Figure 5.8 Comparison between correlation (Method B) and experimental nC_7-nC_{10} liquid mixture thermal conductivity data of Ogiwara (92).

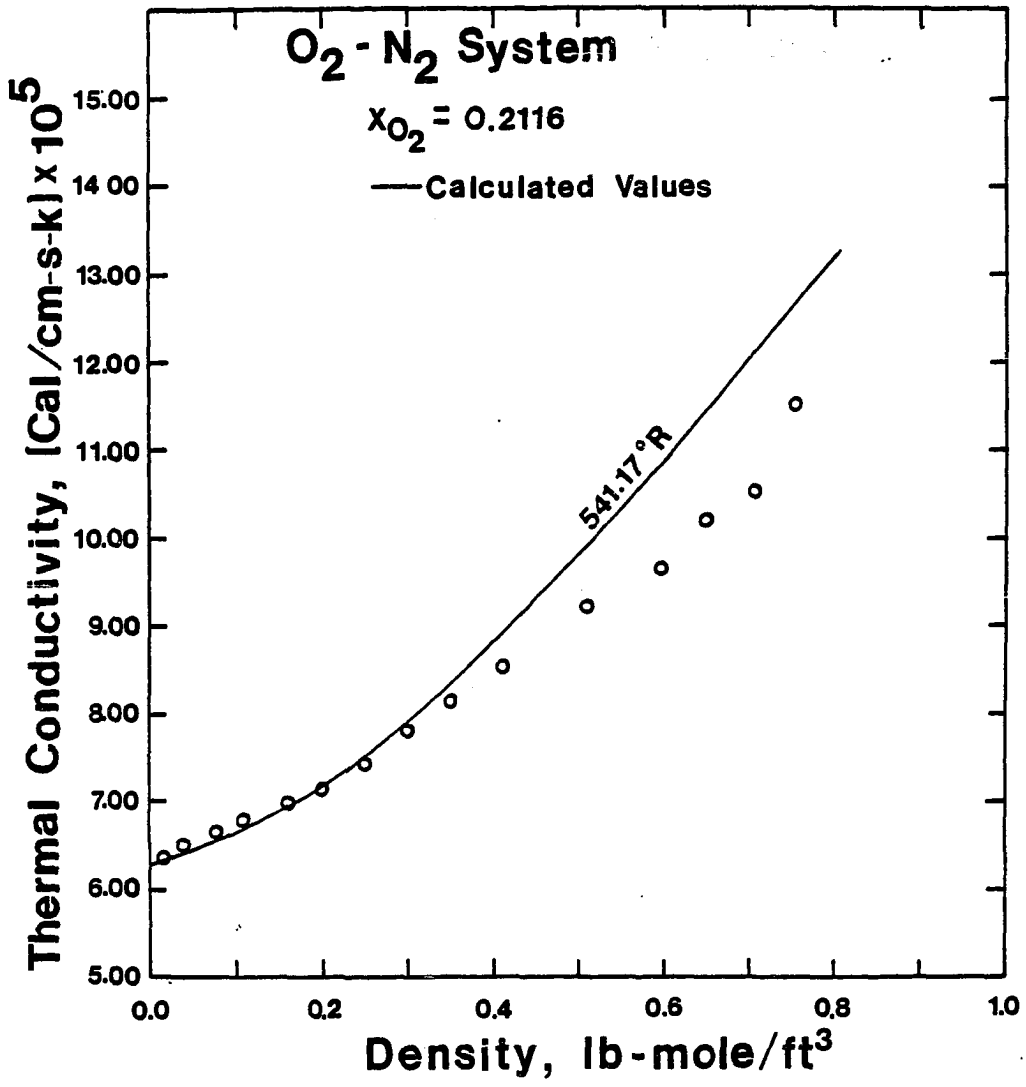

Figure 5.9 Comparison between correlation (Method B) and experimental O_2-N_2 dense gas mixture thermal conductivity data of Fleeter (34).

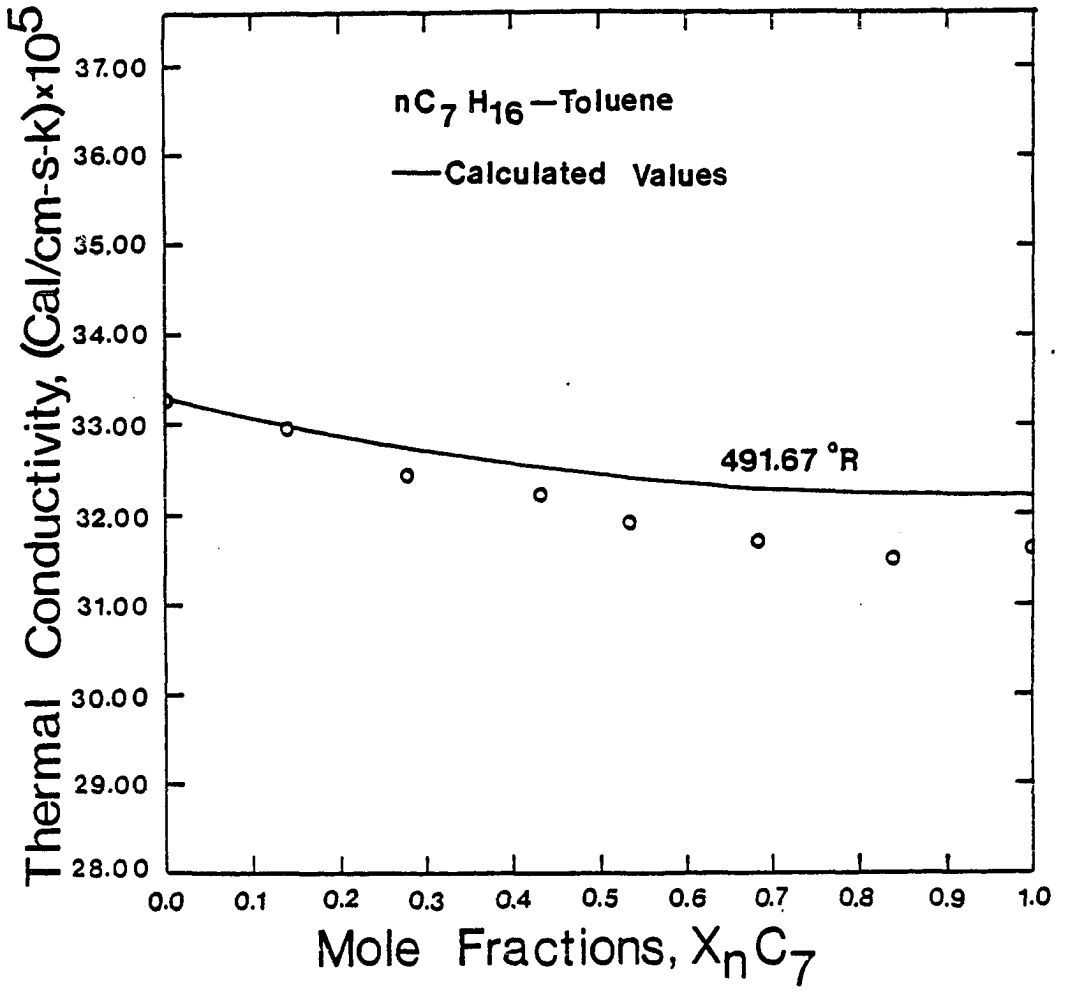

Figure 5.10 Comparison between correlation (Method B) and experimental nC_7-Toluene liquid mixture thermal conductivity data of Parkinson (93).

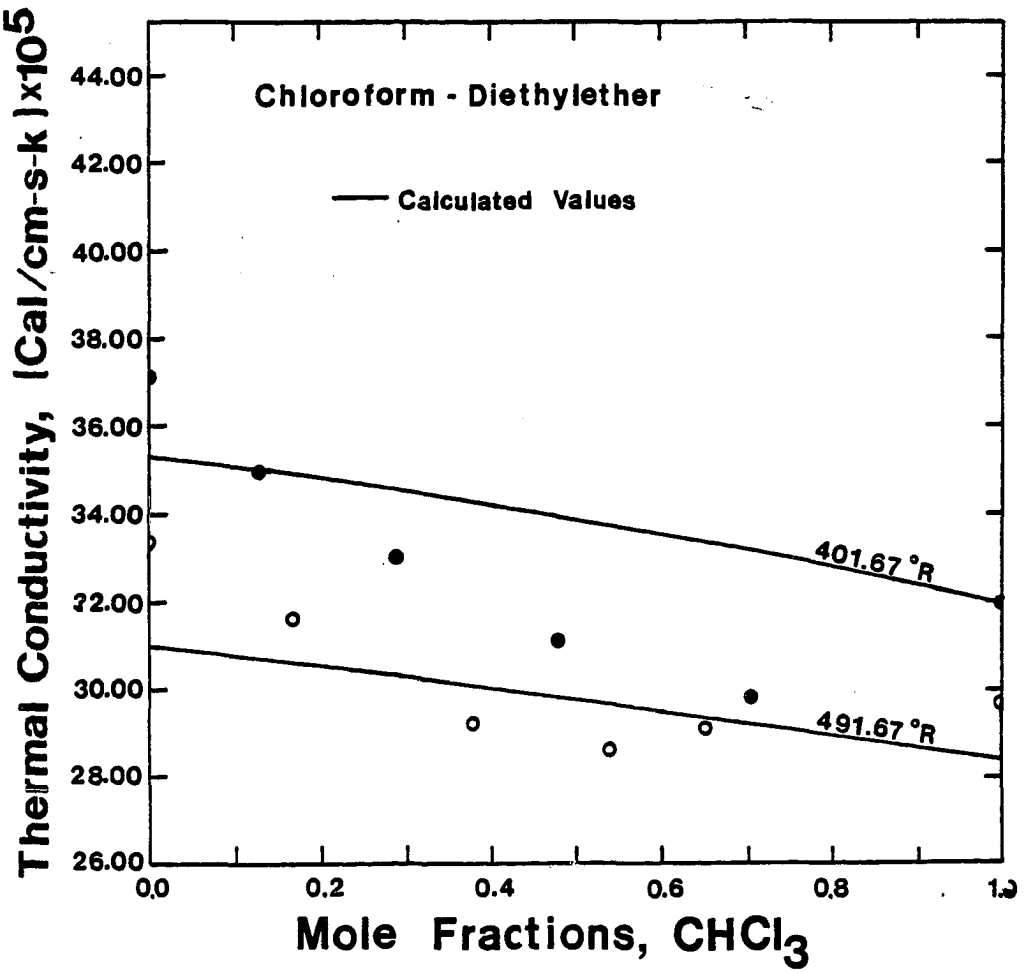

Figure 5.11 Comparison between correlation (Method B) and experimental Chloroform-Diethyl Ether liquid mixture thermal conductivity data of Jamieson (56).

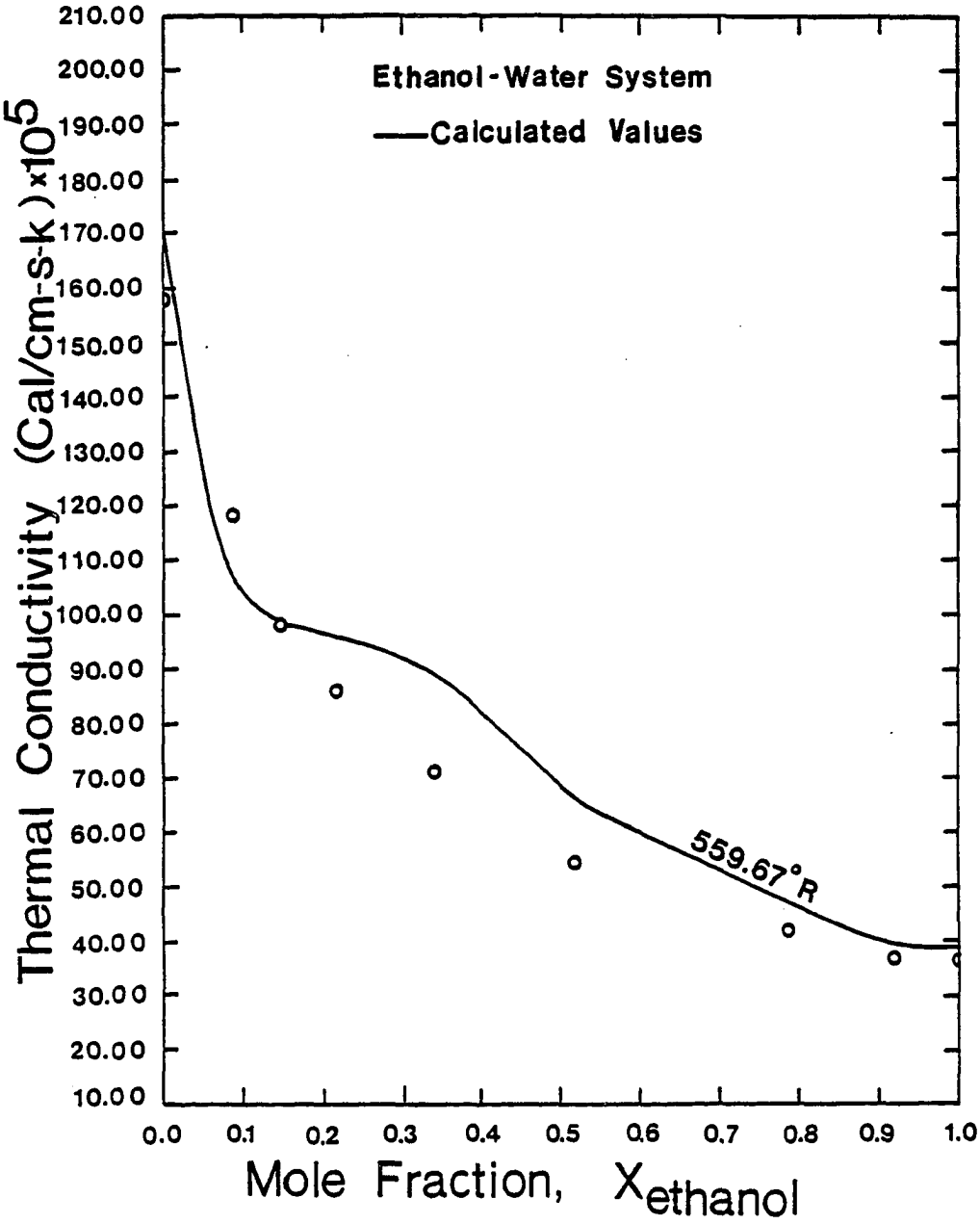

Figure 5.12 Comparison between correlation (Method B) and experimental Ethanol-Water liquid mixture thermal conductivity data of Tsederberg (124).

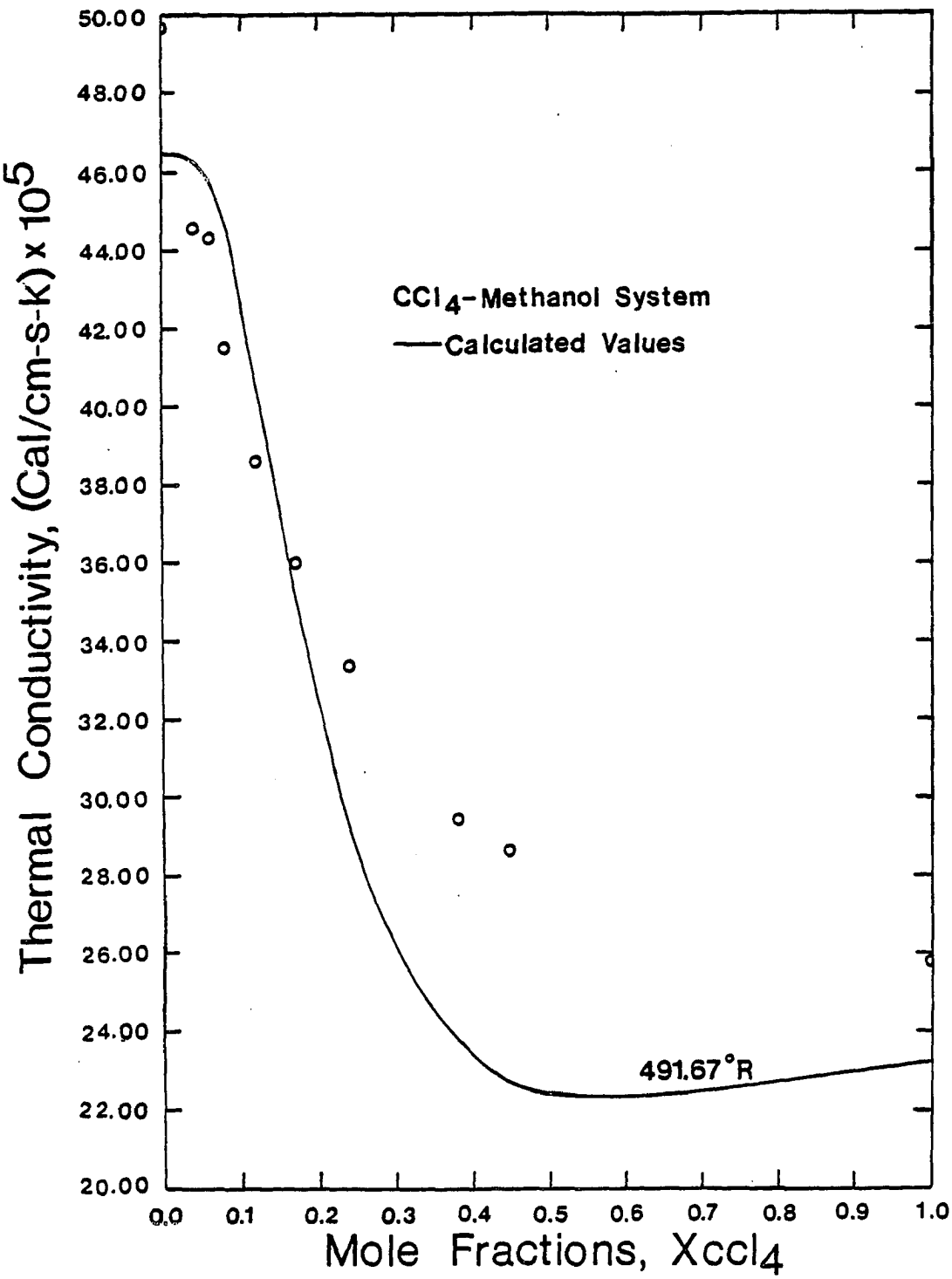

Figure 5.13 Comparison between correlation (Method B) and experimental CCl_4-Methanol liquid mixture thermal conductivity data of Filippov (31).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The conformal solution theory approach provides the design engineer with a simple and easy way of predicting the viscosity and thermal conductivity of binary and multicomponent mixtures in all fluid phases. This approach is superior to all available methods in the literature because the prediction does not depend on the pure components properties as is the case for most other correlations. Also, one multiparameter correlation is used by this approach which covers all possible fluid mixtures in any phase while almost all other correlations are restricted in applications to certain fluid mixtures only, as the literature survey chapter indicates.

Two sets of mixing rules used in this study are equally capable of predicting the characteristic parameters σ_x, ε_x, ω_x, μ_x, κ_x and m^*_x which are required by both the correlations for viscosity and thermal conductivity. The first rules, designated as set A in Table 3.2.1, are the modified van der Waals one fluid mixing rules which are the most widely used because of theoretical significance. The second rules, designated as set B in Table 3.2.1, are the semiempirical exponent mixing rules in which some of the exponents were

determined empirically from experimental thermodynamic data. Method B is a recent one but its accuracy of predictions is as good as method A. This study proves clearly that either set can be applied in the predictions of viscosity and thermal conductivity with the same confidence in accuracy.

Dilute gas mixtures of all possible constituents such as nonpolar, polar and associated fluids are very well predicted without the need of any binary interaction parameters to correct for the unlike-pair separation parameter σ_{ij} and energy parameter ε_{ij}. A value of unity for those parameters is quite satisfactory. The same conclusion is applicable to nonpolar dense gas and liquid mixtures of similar molecular sizes, but as the molecular sizes of the constituents become dissimilar the need arises for binary interaction parameters. This study shows that only one binary interaction parameter for σ_{ij} is sufficient for accurate prediction for dense gas and liquid mixtures of nonpolar constituents. In order to maintain self-consistancy between the thermodynamic and the transport properties, values of the BIPs provided by thermodynamics were used, if available, which in many instances helped to decrease deviations for such mixtures as methane + n-decane, but there is need for a unique set of values determined by simultaneous regression on both thermodynamic and transport properties. This approach is strongly recommended for future research.

Viscosities and thermal conductivities of polar, nonpolar-polar and associated dense gas and liquid mixtures are also predicted reasonably accurately with the use of one binary interaction parameter for σ_{ij}.

To avoid the need for the binary interaction parameters, the empirical model presented in section 3.6 is introduced for viscosity prediction of nonpolar mixtures. This model was successful in predicting hydrocarbon mixture viscosities with high accuracy for mixtures with constituents with molecular weights as large as n-decane. Thus, this empirical model is recommended for viscosity predictions for natural gas and liquified natural gas.

A similar empirical approach should be investigated in future studies for the prediction of thermal conductivity of nonpolar mixtures. Also, the viscosity and thermal conductivity of polar, nonpolar-polar and associated mixtures should be investigated with similar approach to eliminate the need for binary interaction parameters.

Accuracy in the mixtures density is essential for accuracy in prediction of the transport properties, particularly in the dense gas and liquid phases. This is partially the reason for the need of the binary interaction parameter for σ_{ij} which is related to σ_x of the mixture, which in turn

contributes directly to the mixture reduced density. This point clearly indicates the demand for an equation of state which is capable of predicting accurate densities not only for nonpolar mixtures as the BWRS equation of state does, but also mixtures involving polar and associated compounds. This is important point which must be addressed in future research.

The accuracies of the viscosity and thermal conductivity predictions deteriorate considerably for mixtures with association effects. This indicates that no simple mixing rule is capable of predicting the association parameter κ_X for the mixture. This potentially could be attributed in part to the fact that dimerization may take place between the mixture's constituents. Dimerization effects should be considered in any future study, which might lead to a completely different approach than that of the conformal solution theory for associated fluid mixtures. In fact, the approach to association effects should be reconsidered, starting with pure fluid thermodynamics as well as transport properties and continuing through mixture properties. Correlation of the thermophysical properties of associating fluids is a major challenge presently confronting science and engineering.

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