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Correlating Thermal-Conductivity Data for Ternary Liquid Mixtures

Walter W. Focke

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Abstract The performance of several semi-empirical expressions for correlating the temperature, pressure and composition dependence of the thermal conductivity (λ) of pure organic liquids and mixtures was investigated. The temperature and pressure dependence is adequately represented by Chisholm approximants of order (1, 1) or (2, 1) with five and eight adjustable constants, respectively. The fully predictive Vredeveld equation uses mass fractions as the composition variable. It significantly underestimated λ values for the $\mathrm{R32} + \mathrm{R125} + \mathrm{R134a}$ ternary refrigerant system. Binary predictive models with one or two adjustable parameters include the quadratic Scheffé polynomial and its corresponding Padé approximant, the cubic "Margules" model and the theoretical Wassiljewa equation. It was found that the Padé (2, 2) approximant and the Wassiljewa equation satisfactorily correlated the extensive ternary mixture data published by Rowley and coworkers. Best results were obtained when the mole fraction was used as a composition variable. The predictive capability of the models was checked using the $\mathrm{R32} + \mathrm{R125} + \mathrm{R134a}$ ternary refrigerant system. Combining rules were used for cross parameters such that the temperature and pressure dependence was incorporated via the pure fluid properties. Model parameters were fixed using binary data alone. In this case, the quadratic Scheffé, Padé (2, 2), and Wassiljewa (with temperature- and pressure-independent parameters) all provided satisfactory predictions for ternary mixtures.

Keywords Correlation · Liquid thermal conductivity · Scheffé polynomial · Binary · Ternary mixture · Weighted power mean

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W. W. Focke (✉)
Department of Chemical Engineering, Institute of Applied Materials, University of Pretoria,
Lynnwood Road, Pretoria 0001, South Africa
e-mail: walter.focke@up.ac.za

1 Introduction

Heat transfer equipment design requires accurate thermophysical properties data for the working fluids. Such fluids include alkanes employed as heat carriers and thermal storage materials [1] and HFC refrigerants used in refrigeration and heat pump systems [2–14]. The thermal conductivity is a relevant transport property affecting heat transfer performance. Like other fluid physical properties, it is a complex function of temperature, pressure, and composition [15]. Experimental data for ternary mixtures are scarce. Predictive theoretical methods [14–19] are, therefore, indispensable. Nevertheless, empirical and semi-empirical approaches remain important as they may well provide more accurate representations of validated experimental data.

This communication considers semi-empirical approaches for correlating thermal-conductivity data for multicomponent liquid mixtures as a function of pressure, temperature, and composition. Literature methods employed for ternary mixture data are critically reviewed. Alternative approaches are suggested and their performance evaluated using published experimental data. The ultimate objective is to find simple correlating equations with a few (preferably temperature independent and pressure independent) adjustable parameters.

2 Model Development

2.1 Pure-Component Thermal Conductivity

Pure-component liquid thermal conductivity depends on the system temperature and pressure. For data gathered at atmospheric pressure, only the temperature dependence is relevant. Wada et al. [1] found that a linear temperature dependence applies in the case of liquid alkanes:

$$\lambda = a_0 + a_1 T, \tag{1}$$

here λ is the thermal conductivity in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, T is the absolute temperature in K, and the a_i's are constants. According to Yata et al. [2], a linear relationship also holds for the thermal conductivity of refrigerants in the saturated liquid state, but Ro et al. [3] correlated such data using a second-order polynomial:

$$\lambda = a_0 + a_1 T + a_2 T^2 \tag{2}$$

The use of polynomials to approximate functions in a small interval is justified by Taylor's theorem [20]. The coefficients a_k are related to the first derivatives of the thermal conductivity evaluated at an appropriate reference temperature. Taylor polynomials are partial sums or truncated versions of such Taylor series expansions. They tend to provide good approximations for the value of the function near the point of expansion. However, the approximation error of a given Taylor expansion may increase rapidly at points further away.

Padé approximants are rational polynomials used to approximate a function in one variable [21]. They offer greater versatility in representing nonlinear data trends and usually provide superior data fits with the same number of adjustable parameters within an interval of interest [22]. A Padé approximant of order (m, n), in temperature as the variable, is defined by:

$$\lambda = \frac{a_0 + a_1 T + a_2 T^2 + \cdots + a_m T^m}{1 + b_1 T + b_2 T^2 + \cdots + b_n T^n} \tag{3}$$

Note that, following the standard convention, the leading coefficient of the denominator polynomial is set equal to unity. According to Gerald [23], the most useful Padé approximants are those where the order of the numerator polynomial is the same or one greater than the degree of the denominator polynomial. A Padé approximant of order (1, 1) is expected to perform equally well or better than the quadratic Taylor polynomial defined by Eq. 2:

$$\lambda = \frac{a_0 + a_1 T}{1 + b_1 T} \tag{4}$$

For refrigerants, several investigators [2–8] represented the combined temperature and pressure dependence, of pure and specific binary and ternary refrigerant mixtures, by the following polynomial:

$$\lambda = \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} T^i P^j \tag{5a}$$

An equivalent matrix product form is

$$\lambda = \left(1, T, T^2\right) \begin{bmatrix} a_{00} & a_{01} & a_{02} \\ a_{10} & a_{11} & a_{12} \\ a_{20} & a_{21} & a_{22} \end{bmatrix} \begin{pmatrix} 1 \\ P \\ P^2 \end{pmatrix} \tag{5b}$$

Equation 5 has nine adjustable coefficients, and thus, much experimental effort is required for their determination. Jeong et al. [11] reduced the number of parameters to be fitted by arbitrarily setting the coefficients for the cross terms TP and T^2P^2, i.e., a_{11} and a_{22}, equal to zero. The number of adjustable constants can be trimmed to as few as five if Eq. 5 can be factored as follows:

$$\lambda = \left(b_0 + b_1 T + b_2 T^2\right)\left(1 + c_1 P + c_2 P^2\right) \tag{6}$$

This implies that

$$\begin{bmatrix} a_{00} & a_{01} & a_{02} \\ a_{10} & a_{11} & a_{12} \\ a_{20} & a_{21} & a_{22} \end{bmatrix} = \begin{bmatrix} b_0 & b_0 c_1 & b_0 c_2 \\ b_1 & b_1 c_1 & b_1 c_2 \\ b_2 & b_2 c_1 & b_2 c_2 \end{bmatrix} \tag{7}$$

Temperature and pressure are independent variables, and therefore, the second-order bivariate Taylor polynomial, with six adjustable parameters, has a more rigorous mathematical foundation:

$$\lambda = \sum_{i=0}^{2} \sum_{j=0}^{2-i} a_{ij} T^i P^j = a_{00} + a_{01} P + a_{02} P^2 + a_{10} T + a_{11} TP + a_{20} T^2 \tag{8}$$

Again, it is expected that a rational function in two variables would provide superior data representation of a function inside a finite domain. Such Padé rational polynomials in two variables are also called Chisholm approximants. As for Padé, it is anticipated that Chisholm approximants with the same number of adjustable coefficients will perform better than simple multivariate Taylor polynomial expansions. The Chisholm approximants of orders (1, 1) and (2, 1) are defined by Eqs. 9 and 10, respectively:

$$\lambda = \frac{a_0 + a_1 T + a_2 P}{1 + b_1 T + b_2 P} \tag{9}$$

$$\lambda = \frac{a_0 + a_1 T + a_2 P + a_{11} T^2 + a_{12} TP + a_{22} P^2}{1 + b_1 T + b_2 P} \tag{10}$$

2.2 Mixture Thermal Conductivity

From an engineering point of view, the mixture composition can be expressed in any convenient manner. The technical literature reveals a distinct preference for the use of mass fractions to correlate the effect of composition on liquid thermal conductivity [1–14]. However, from a thermodynamic perspective, the use of mole fractions seems more appropriate. Independent of whether volume (φ_i), mass (w_i), or mole (x_i) fractions are used to characterize composition, the corresponding fractions are subject to the restrictions:

$$0 \le z_i \le 1 \quad \text{and} \quad \Sigma z_i = 1 \tag{11}$$

where $z \in \{\varphi, w, x\}$ and the summation is over the n distinct components making up the mixture.

The "linear blending rule" provides the simplest concentration dependence. It states the general expectation that mixture properties vary linearly with composition:

$$\lambda \equiv \sum_{i=1}^{n} \lambda_i z_i = \lambda_1 z_1 + \lambda_2 z_2 \ldots \lambda_n z_n \tag{12}$$

In Eq. 12, n is the number of components in the mixture, λ_i denotes the pure component property value and z_i the volume, mass, or mole fraction of component i in the mixture. The linear blending rule is a predictive equation, since there are no adjustable parameters in the correlation. It represents a weighted arithmetic mean over the pure-component properties. Weighted power means provide a more general approach to predictive correlation equations. The power mean of order p is defined as follows:

$$\lambda^p = \sum_{i=1}^{n} \lambda_i^p z_i = \lambda_1^p z_1 + \lambda_2^p z_2 \ldots \lambda_n^p z_n \quad (p \neq 0)$$

$$\lambda = \prod_{i=1}^{n} \lambda_i^{z_i} = \lambda_1^{z1} \lambda_2^{z2} \ldots \lambda_n^{z_n} \quad (p = 0) \tag{13}$$

Spindler et al. [13] found that choosing $p = -0.65$ and using mass fractions as composition variables provides good agreement between predictions and the experimental data for the ternary mixture R407C.

Poling et al. [14] reviewed empirical equations for predicting binary liquid mixture thermal conductivity. Some methods are limited to binary mixtures as they can not be extended to ternary or higher mixtures, while others are complicated and/or need additional information [24,25]. Poling et al. [14] found that the better methods show comparable performance for binary mixtures. The simplest of these is the inverse root-mean-square mixing rule, i.e., with $p = -2$ in Eq. 13, first enunciated by Vredeveld in 1973 [14].

Several investigators [3–5,7,10] effectively fit binary refrigerant mixture data to polynomial expansions of the form,

$$\lambda = \sum_{i=0}^{2} \sum_{j=0}^{2} \sum_{k=0}^{2} a_{ijk} T^i P^j w_1^k \tag{14}$$

here w_1 represents the mass fraction of component 1 in the binary mixture, T is the absolute temperature in K, and P is the pressure in bar. In expanded form, this equation reads

$$\lambda = \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij0} T^i P^j + w_1 \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij1} T^i P^j + w_1^2 \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij2} T^i P^j \tag{15}$$

This equation for a binary mixture has 27 adjustable coefficients a_{ijk}. Pure-component 1 and pure-component 2 behavior are indicated by $w_1 = 1$ and $w_1 = 0$, respectively. In these two cases, the equation reduces to the following two limiting forms, respectively:

$$\lambda_1 = \lambda_{w_1=1} = \sum_{i=0}^{2} \sum_{j=0}^{2} \left(a_{ij0} + a_{ij1} + a_{ij2}\right) T^i P^j \tag{16}$$

$$\lambda_2 = \lambda_{w_1=0} = \sum_{i=0}^{2}\sum_{j=0}^{2} a_{ij0} T^i P^j \tag{17}$$

Both these equations are of the form defined by Eq. 5 for pure refrigerants. Thus, of the 27 adjustable coefficients in Eq. 15, 18 are established by the pure-component behavior and the remaining nine are determined from binary data.

Gao et al. [7] proposed the following model for binary mixtures:

$$\lambda = \sum_{i=0}^{2}\sum_{j=0}^{2} a'_{ij0} T^i P^j \left[1 + w_1 \sum_{i=0}^{2}\sum_{j=0}^{2} a'_{ij1} T^i P^j + w_1^2 \sum_{i=0}^{2}\sum_{j=0}^{2} a'_{ij2} T^i P^j\right] \tag{18}$$

In this case, the pure component 2 behavior is obtained with $w = 0$ as before. However, for $w = 1$ an entirely different temperature and pressure polynomial results with exponents up to $T^4 P^4$. Equation 18 is, therefore, a less satisfactory option for representing binary mixture data.

Equation 14, as shown more clearly by Eq. 15, effectively implies quadratic composition dependence for the thermal conductivity. Unfortunately in the format presented, it is not clear how this model could be extended to ternary and higher mixtures. Subsequently, Jeong et al. [11] proposed the following expression for ternary refrigerant mixtures:

$$\begin{aligned}\lambda &= w_1\lambda_1 + w_2\lambda_2 + w_3\lambda_3 + \alpha_{12} w_1 w_2 \sqrt{\lambda_1\lambda_2}\\ &\quad + \alpha_{13} w_1 w_3 \sqrt{\lambda_1\lambda_3} + \alpha_{23} w_2 w_3 \sqrt{\lambda_2\lambda_3}\\ &\quad + \left(\varepsilon_1 w_1 w_2 w_3 + \varepsilon_2 w_1^2 w_2^2 w_3^2 + \varepsilon_3 w_1^3 w_2^3 w_3^3\right)\sqrt[3]{\lambda_1\lambda_2\lambda_3},\end{aligned} \tag{19}$$

here the α_{ij} and the ε_i are temperature-independent coefficients. This proposal has several attractive features: firstly, pure-component properties are unambiguously recovered when the corresponding mass fraction is set equal to unity ($w_i = 1$); and second, the temperature and pressure dependence of the mixture is determined entirely by that of the pure components. That means that no new temperature functions need to be introduced in order to describe their effect on the properties of the ternary mixture. A drawback of this proposal is that while the composition dependence is quadratic for binary mixtures, this is not the case for the ternary mixture with the model containing composition terms up to the ninth order! These higher coefficients require ternary data for their evaluation.

The above observations point to a need for improved models to represent thermal-conductivity composition dependence. Engineers prefer fully predictive models but will settle for binary predictive models when these are not accurate enough. The latter are models that feature parameters that, in principle at least, are fully determined once data for binary mixtures are at hand. To this end two general approaches are considered here: Scheffé polynomials [26,27] and their rational polynomial extensions [28] and the general power mean mixture model [29].

2.3 Scheffé Polynomials and Padé Approximants as Mixture Rules

Scheffé polynomials are in essence Taylor polynomial expansions in composition that take the simplex constraint, Eq. 11, into account [26]. The homogeneous quadratic form for a ternary mixture is [27]

$$\lambda = \lambda_{11}x_1^2 + \lambda_{22}x_2^2 + \lambda_{33}x_3^2 + 2\lambda_{12}x_1x_2 + 2\lambda_{13}x_1x_3 + 2\lambda_{23}x_2x_3 \tag{20}$$

Note that this equation has only one adjustable parameter per binary in the mixture. Suitable Padé approximants corresponding to rational extensions of Scheffé polynomials may be defined as ratios of homogeneous Scheffé polynomials [28]. The binary-predictive requirement apparently limits one to quadratic polynomials (or lower) forms:

$$\lambda = \frac{a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2 + 2a_{12}x_1x_2 + 2a_{13}x_1x_3 + 2a_{23}x_2x_3}{b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + 2b_{12}x_1x_2 + 2b_{13}x_1x_3 + 2b_{23}x_2x_3} \tag{21}$$

Note that the pure-component thermal conductivity is now given by the ratio $\lambda_i = a_{ii}/b_{ii}$. While other approaches nay hold promise [28], for convenience, it is arbitrarily assumed here that $b_{ii} = 1\,\forall\, i$, i.e.,

$$\lambda = \frac{\lambda_{11}x_1^2 + \lambda_{22}x_2^2 + \lambda_{33}x_3^2 + 2\lambda_{12}x_1x_2 + 2\lambda_{13}x_1x_3 + 2\lambda_{23}x_2x_3}{x_1^2 + x_2^2 + x_3^2 + 2b_{12}x_1x_2 + 2b_{13}x_1x_3 + 2b_{23}x_2x_3} \tag{22}$$

The cross parameters in Eqs. 20–22 are expected to be functions of temperature and pressure. Thus, one would need binary data over the full temperature and pressure range to fully determine λ_{ij}. This predicament can be overcome by postulating suitable combining rules as discussed later.

2.4 Weighted Power Mean Mixture Model

An alternative approach is provided by the weighted power mean mixture model [29]. The essence of this model can be summarized as follows: intermolecular interactions have an extremely short range. This justifies the assumption that only binary molecular interactions need to be considered. In this context, a liquid mixture may be viewed as an assembly of hypothetical clusters defined by the nature of a central molecule together with its nearest neighbors. Every fluid physical property, e.g., thermal conductivity λ, is ultimately determined by binary interactions between the central molecules and their neighbors in the cluster. The effect of these interactions, on the values that the physical property will assume, is captured by a matrix of binary coefficients $L = [\lambda_{ij}]$. The following notation is used: the subscript i indicates the nature of the central molecule in the cluster and j the nature of a neighboring molecule. In a pure component i fluid, all the interactions are identical and their effect on the thermal conductivity is described by the parameter λ_{ii}. It immediately follows that λ_{ii} is equivalent to the thermal conductivity of the pure component i, i.e., $\lambda_{ii} = \lambda_i$.

In this context, a mixture model is defined once prescriptions for (i) estimating fluid cluster properties, and (ii) ways of combining them to yield an overall mixture property, are given. A particularly flexible form is obtained when both prescriptions entail global composition-weighted power means [29]. The cluster property is expressed as a composition-weighted power mean of order s over the cluster interactions λ_{ij}:

$$\begin{aligned} u_i(x) &= \left(\sum_{k=1}^{n} x_k \lambda_{ik}^{s}\right)^{1/s} \quad (s \in \mathbb{R}, s \neq 0) \\ u_i(x) &= \prod_{k=1}^{n} \lambda_{ik}^{x_k} \qquad\qquad (s = 0) \end{aligned} \tag{23}$$

The overall fluid property is given by a weighted power mean of order r over the cluster properties:

$$\begin{aligned} \lambda &= \left(\sum_{i=1}^{n} x_i [u_i(x)]^{r}\right)^{1/r} \quad (r \in \mathbb{R}, r \neq 0) \\ \lambda &= \prod_{i=1}^{n} (u_i(x))^{x_i} \qquad\qquad (r = 0) \end{aligned} \tag{24}$$

For $r, s \neq 0$, the weighted power mean mixture model takes the form,

$$\lambda = \left[\sum_{i=1}^{n} x_i \left(\sum_{j=1}^{n} x_j \lambda_{ij}^{s}\right)^{r/s}\right]^{1/r} \tag{25}$$

Equation 25 only features binary adjustable parameters. Thus, in principle at least, it predicts multicomponent behavior from knowledge of pure component and binary mixture data. Furthermore, Eq. 25 is a generalized model form as it includes several other well-known mixture models, e.g., quadratic and cubic Scheffé polynomials, etc., as special cases [29]. For example, the quadratic Scheffé polynomial is obtained setting $s = r = 1$. For a ternary mixture, it reads

$$\begin{aligned} \lambda = {} & \lambda_{11} x_1^2 + \lambda_{22} x_2^2 + \lambda_{33} x_3^2 + (\lambda_{12} + \lambda_{21})\, x_1 x_2 + (\lambda_{13} + \lambda_{31})\, x_1 x_3 \\ & + (\lambda_{23} + \lambda_{32})\, x_2 x_3 \end{aligned} \tag{26}$$

Comparing coefficients with Eq. 20 shows that $\lambda_{ij} = \lambda_{ji}$ for Scheffé polynomials. The cubic homogeneous Scheffé polynomial for a ternary mixture is defined by

$$\begin{aligned} \lambda = {} & \lambda_{111} x_1^3 + \lambda_{222} x_2^3 + \lambda_{333} x_3^3 + 3\lambda_{112} x_1^2 x_2 + 3\lambda_{122} x_1 x_2^2 + 3\lambda_{113} x_1^2 x_3 \\ & + 3\lambda_{133} x_1 x_3^2 + 3\lambda_{223} x_2^2 x_3 + 3\lambda_{233} x_2 x_3^2 + 6\lambda_{123} x_1 x_2 x_3 \end{aligned} \tag{27}$$

Ternary mixture data are required to fix the value of the ternary constant λ_{123}. It cannot be determined from binary data alone. The desire that knowledge of pure and binary data should suffice to fix model parameters apparently disqualifies this and other higher-order Scheffé polynomials from consideration. However, the general power mean mixture model yields nth order Scheffé K-polynomials, with two constants per binary, if one sets $r = 1$ and $s = 1/(n-1)$. For example, $n = 3$ (i.e., $s = 1/2$) yields a cubic Scheffé polynomial. Expansion of the formula, collecting terms, and comparing the coefficients with those in Eq. 28 reveals that

$$\lambda_{iii} = \lambda_{ii} = \lambda_i \tag{28}$$

and

$$\lambda_{ijk} = \frac{1}{3}\left(\sqrt{\lambda_{ij}\lambda_{ik}} + \sqrt{\lambda_{ji}\lambda_{jk}} + \sqrt{\lambda_{ki}\lambda_{kj}}\right) \tag{29}$$

Setting $r = 1$ and $s = -1$ in Eq. 25 yields the following expression:

$$\lambda = \sum_{i=1}^{n} \frac{x_i}{\sum_{j=1}^{n} x_j/\lambda_{ij}} \tag{30}$$

Defining $\Lambda_{ij} = \lambda_{ii}/\lambda_{ij}$, Eq. 30 may be rearranged to yield the familiar form of the theoretical Wassiljewa [30] expression for the thermal conductivity of dilute hard-sphere gases:

$$\lambda = \sum_{i=1}^{n} \frac{\lambda_{ii} x_i}{\sum_{j=1}^{n} \Lambda_{ij} x_j} \tag{31}$$

Dey et al. [31] recently drew attention to the utility of the Wassiljewa model for the correlation of isothermal liquid mixture conductivity.

2.5 Combining Rules for Cross Parameters

Combining rules express cross parameters in terms of pure-component properties. Equation 31 was initially derived for the thermal-conductivity data of dilute gases. For this situation, the Λ_{ij} are connected to molecular properties by the following combining rule [15]:

$$\Lambda_{ij} = \left(\frac{\sigma_i + \sigma_j}{2\sigma_i}\right)^2 \sqrt{\frac{M_i + M_j}{2M_j}} \tag{32}$$

Here σ_i is the molecular radius and M_i is the molar mass of molecular species i. Equation 32 states that the Λ_{ij} only depends on molecular properties, i.e., fundamentally they are temperature- and pressure-independent parameters. This suggests the following combining rule for the temperature-pressure dependence of the cross parameters of the weighted power mean mixture model:

$$\lambda = \left[\sum_{i=1}^{n} \lambda_{ii}^{r} x_i \left(\sum_{j=1}^{n} x_j \Lambda_{ij}^{-s} \right)^{r/s} \right]^{1/r} \tag{33}$$

In effect, it is assumed that the temperature dependence for properties of cluster i is the same as that for pure component i. For the Scheffé model, where $r = 1$ and $s = 1$, the combining rule becomes

$$2\lambda_{12} = \lambda_{11}/\Lambda_{12} + \lambda_{22}/\Lambda_{21} \tag{34}$$

Note that, with this combining rule, the Scheffé model effectively has two adjustable parameters per binary.

Dey et al. [31] also proposed a fully predictive version for Eq. 31 by expressing Λ_{ij} as follows:

$$\Lambda_{ij} = \frac{1}{4} \left[1 + \sqrt{\frac{\lambda_{ii}}{\lambda_{jj}}} \left(\frac{M_i}{M_j} \right)^{3/8} \right]^2 \tag{35}$$

However, since the λ_{ii} are temperature and pressure dependent, their proposal also makes the Λ_{ij} functions of temperature and pressure. It was, therefore, not considered here.

The geometric combining rule provides an alternative for quadratic Scheffé polynomials and Padé approximants:

$$\lambda_{ij} = \alpha_{ij} \sqrt{\lambda_{ii} \lambda_{jj}} \tag{36}$$

here the α_{ij} are deemed to be temperature- and pressure-independent constants. This combining rule reduces the Scheffé polynomial (18) to the equation proposed by Jeong et al. [11] for binary refrigerant mixtures. It also provides a general and consistent framework for multicomponent mixtures showing quadratic composition dependence. A fully predictive Scheffé mixing rule version is obtained when $\alpha_{ij} = 1 \, \forall \, i, j$ for the cross terms in Eq. 26.

3 Model Testing: Results and Discussion

Table 1 lists the liquid mixture thermal-conductivity datasets used in this study. The purpose of regression is to find the model that "best" fits the observations. This requires model parameter estimates (coefficient matrix L) such that some predetermined criterion is satisfied. Minimization of the sum of squares of the residuals was chosen for the present analysis:

$$S(L) = \sum_{k=1}^{N} \varepsilon_k^2 = \sum_{k=1}^{N} \left[y_k - \hat{y}_k(L, x_k) \right]^2 \tag{37}$$

Table 1 Liquid mixture thermal-conductivity datasets

System	Description	T (°C) P (bar)	Number of datasets (data points)	References
I	2,2,4-Trimethylpentane, 2-butanone, 2-propanol, benzene, carbon tetrachloride, chloroform, cyclohexane, *n*-butanol, *n*-butyl acetate, *n*-heptane, *n*-hexane, *n*-pentane, *n*-propanol, and toluene	25 °C Ambient pressure	B[a]: 47 (62) T[b]: 14 (168)	[25,32]
II	2,2,4-Trimethylpentane, benzene, carbon tetrachloride, cyclohexane, *n*-heptane, *n*-hexane, and toluene	40 °C Ambient pressure	B: 20 (21) T: 7 (46)	[33]
III	Liquid paraffin mixture: heptane, dodecane, and hexadecane	(20–90) °C Atmospheric pressure	B: 3 (54) T: 1 (18)	[1]
IV	Refrigerants R22 (chlorodifluoromethane), R142b (1-chloro-1,1-difluoroethane), and R152a (1,1-difluoroethane)	(−50 to 50) °C (2.1–20.1) bar	B: 6 (125)	[5]
V	Refrigerants R32 (difluoromethane), R125 (pentafluoroethane), and R134a (1,1,1,2-tetrafluoroethane)	(−50 to 80) °C (2–30) bar	B: 3 (434) T: 1 (212)	[2–4,6–8,10,11]

[a] B: Number of binary datasets
[b] T: Number of ternaries

The performance of Eqs. 5–10 to represent $\lambda = \lambda(T, P)$ was tested using experimental data for the pure refrigerants R22, R32, R125, R134a, R142b, and R152a. The results are shown in Table 2. The uncertainty in the experimental data may be as much as 2 % [3,4,10]. Taking this into consideration, the Chisholm (1, 1) model, Eq. 9, adequately correlated the experimentally determined temperature and pressure dependence for all refrigerants except perhaps R125. This model has four fewer parameters than the conventional matrix model, Eq. 5, and one less adjustable parameter than the Taylor expansion, Eq. 8, yet provided comparable correlating performance. Table 3 gives the values for the model parameters and the temperature and pressure ranges for refrigerants R32, R125, and R134a. Note that the data for R125 are better fitted by Eq. 10. See Table 2 and Fig. 1.

Table 4 and Figs. 2 and 3 show the performance of the various mixture rules with respect to correlating the composition dependence of the isothermal-isobaric data for System I. Deviations from the predictions of the linear blending rule were not large in this case. The maximum deviation is only 15 %. The linear blending rule and the

Table 2 Performance comparison for the temperature and pressure correlations for pure refrigerants [3,4,6,10]

Model	Equation number	Adjustable parameters	Absolute average deviations (AAD) (%)					
			R22 Average (max)	R32 Average (max)	R125 Average (max)	R134a Average (max)	R142b Average (max)	R152a Average (max)
Matrix	5	9	0.21 (0.74)	0.35 (2.32)	0.56 (1.95)	0.29 (0.72)	0.30 (0.84)	0.11 (0.31)
Chisholm (2, 1)	10	8	0.23 (0.82)	0.34 (1.54)	0.55 (1.78)	0.29 (0.71)	0.29 (0.89)	0.12 (0.32)
Taylor (2)	8	6	0.23 (1.05)	0.87 (5.15)	0.72 (2.34)	0.29 (0.72)	0.31 (0.85)	0.13 (0.34)
Product	6	5	1.27 (5.27	1.29 (7.90)	2.81 (12.33)	1.10 (4.47)	0.85 (2.13)	0.71 (2.34)
Chisholm (1, 1)	9	5	0.23 (0.86)	0.34 (2.11)	0.83 (2.39)	0.31 (0.79)	0.30 (0.97)	0.13 (0.48)

Table 3 Thermal-conductivity data for R32 [3, 4], R125 [6, 10], and R134a [3,10] fitted with Eq. 9

Refrigerant	R32	R125	R134a
Number of data points	48	56	49
T range (K)	223.15–323.15	193.5–333.9	223.15–323.25
P range (bar)	2–20	2–30	2–20
Coefficients, Eq. 6			
a_0	2.970×10^{-1}	1.950×10^{-1}	2.553×10^{-1}
a_1	-7.258×10^{-4}	-9.473×10^{-4}	-4.776×10^{-4}
a_2	1.584×10^{-3}	1.106×10^{-3}	2.338×10^{-3}
a_{11}	–	1.155×10^{-6}	–
a_{22}	–	5.413×10^{-7}	–
a_{12}	–	-1.708×10^{-6}	–
b_1	-1.256×10^{-3}	-2.463×10^{-3}	1.326×10^{-3}
b_2	6.120×10^{-3}	5.284×10^{-3}	1.520×10^{-2}
AAD (%)	0.34	0.53	0.31
Max error (%)	2.10	1.78	0.78

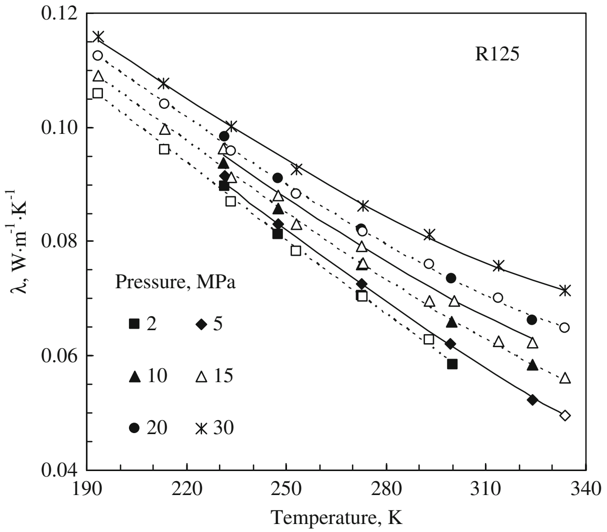

Fig. 1 Effect of temperature and pressure on the thermal conductivity of liquid R125 correlated with the Chisholm (2, 1) model defined by Eq. 10: data from Gao et al. [6] (open symbols) and Jeong et al. [4,10] (solid symbols). Lines indicate predictions of Eq. 10

Vredeveld equations worked better when mass fractions were used as the composition variable. Mole fractions provided better correlative performance for the Padé (2, 2) and Wassiljewa models, while for the Scheffé model the performance was similar. The Wassiljewa and Padé (2, 2) models performed best with maximum and average absolute deviations of 2.4 % and 0.4 %, respectively. Similar comments apply to the data for System II with experimental values determined at 40 °C. Figure 3 illustrates the performance of the Vredeveld and Wassiljewa models. Here the AAD was less than 0.3 % and the maximum deviation was less than 2 %. The predictive Margules model,

Table 4 Comparing thermal-conductivity mixture models for isothermal System I [25,32]

Mixing rule	AAD (%)	Mass basis		Mole basis	
	No. parameters	Average	Maximum	Average	Maximum
Linear blending rule	–	3.88	9.60	6.23	14.74
Vredeveld	–	2.19	9.56	4.13	9.86
Scheffé (2)	1	0.58	3.31	0.55	3.51
Margules[a] (2)	2	0.39	2.95	0.43	3.08
Padé (2, 2)	2	0.57	2.5	0.39	2.31
Wassiljewa	2	0.43	3.12	0.38	2.39

[a] Binary predictive version with ternary constant defined by Eq. 29

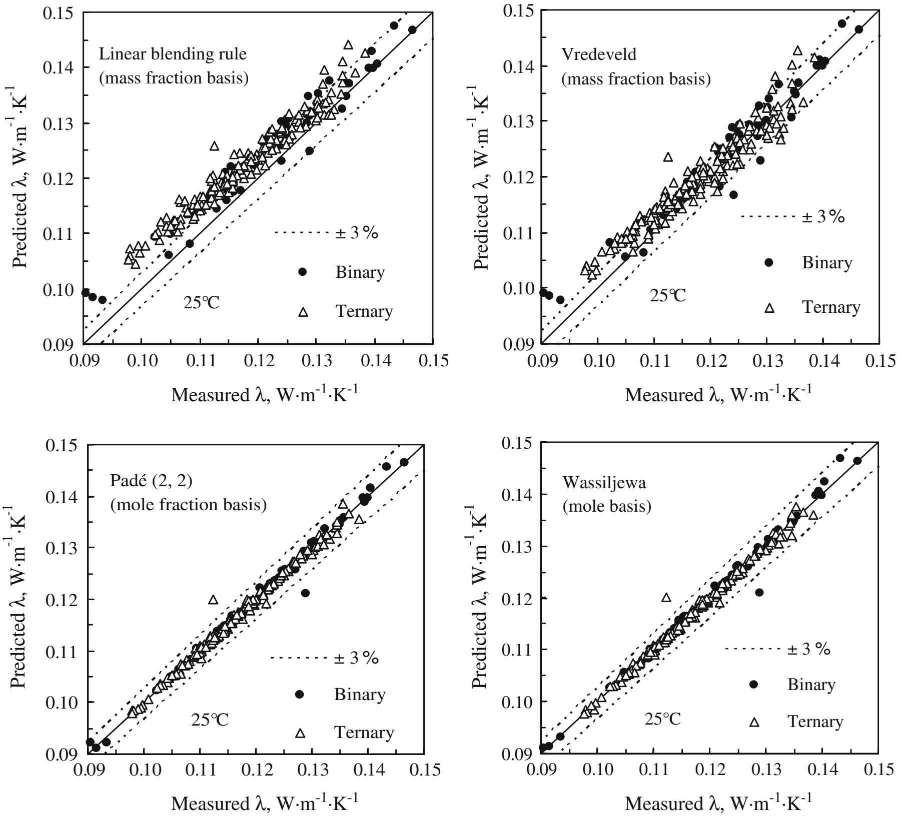

Fig. 2 Performance comparison of the linear blending rule, Vredeveld, Padé (2, 2), and Wassiljewa models for correlating the composition dependence of thermal-conductivity data at 25 °C for System I [25,32]

Eq. 27 together with Eq. 29, did not offer advantages over the Wassiljewa model and was not further considered.

Table 5 and Fig. 4 show the performance of various models with respect to the liquid paraffin data [1]. The two combining rule options for the binary cross parameters were compared. The adjustable parameters were determined using only the pure and binary

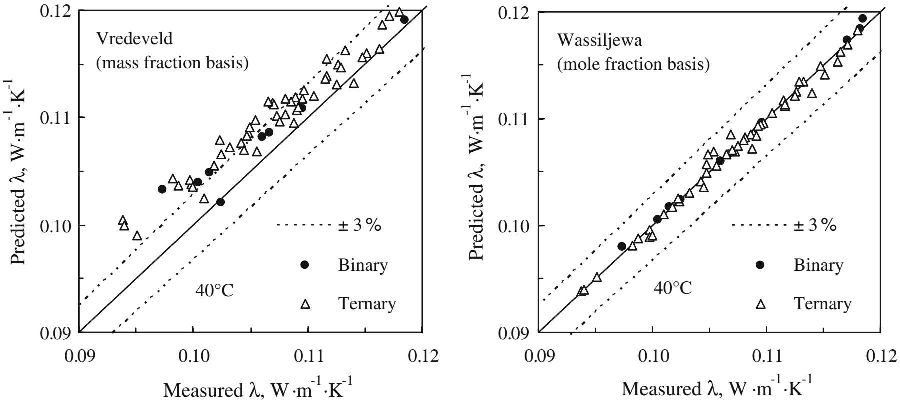

Fig. 3 Performance of the Vredeveld and Wassiljewa models for correlating the isothermal (40 °C) thermal-conductivity data of System II [33]

Table 5 Comparing thermal-conductivity mixture models for liquid paraffin mixtures (System III) [1]

Mixing rule	AAD (%) No. parameters	Mass basis Average	Mass basis Maximum	Mole basis Average	Mole basis Maximum
Linear blending rule	–	0.64	2.12	2.28	5.55
Vredeveld	–	1.21	3.22	0.42	1.49
Scheffé (2)[a]					
Binary	1	0.37	1.71	0.58	2.18
Ternary		0.59	1.26	0.75	1.40
Scheffé (2)[b]					
Binary	2	0.37	1.46	0.58	1.95
Ternary		0.55	1.49	0.50	1.53
Padé (2, 2)[a]					
Binary	2	0.36	1.17	0.41	1.35
Ternary		0.37	0.93	0.37	1.09
Wassiljewa					
Binary	2	0.36	1.43	0.37	1.46
Ternary		3.39	5.12	0.50	1.27

Ternary data predicted from model parameter fit using binary data where applicable

[a] Geometric combining rule (Eq. 34)

[b] Combining rule of Eq. 36

mixture property data. Ternary values were predicted and compared to experiment. The linear blending rule did well when mass fractions were used as the composition variable. It even outperformed the Vredeveld correlation. The mass fraction-based Padé (2, 2) model did best, but was only marginally better than the quadratic Scheffé model with the cross parameters defined by the geometric combining rule.

Table 6 shows the correlation results for the binary mixtures of R22 with either R142b or R152a. Neither the linear blending rule nor the Vredeveld equation did well here. However, the data were very well correlated with the second-order Scheffé model, especially so when the combining rule of Eq. 34 was used. The Padé

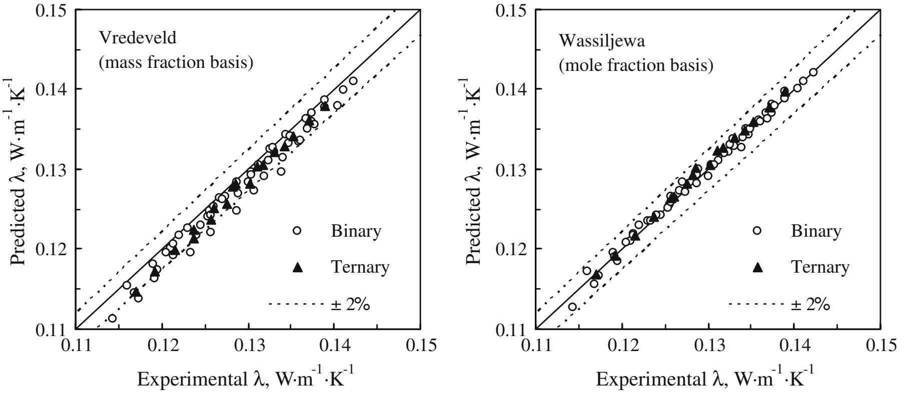

Fig. 4 Performance of the Vredeveld and Wassiljewa models for correlating the thermal-conductivity data for the ternary mixture of heptane, dodecane, and hexadecane [1]

Table 6 Comparing thermal-conductivity mixture models for binary blends of refrigerant R22 with either R142b or R152a (System IV) [5]

Mixing rule	AAD (%)	Mass basis		Mole basis	
	No. parameters	Average	Maximum	Average	Maximum
Linear blending rule	–	2.26	4.83	2.82	5.03
Vredeveld	–	1.82	4.72	2.29	4.91
Scheffé (2)[a] Binary	1	0.44	1.33	0.48	1.78
Scheffé (2)[b] Binary	2	0.31	1.16	0.31	0.96
Padé (2, 2)[a] Binary	2	0.42	1.37	0.48	1.60
Wassiljewa Binary	2	0.39	1.60	0.39	1.59

[a] Geometric combining rule (Eq. 34)

[b] Combining rule of Eq. 36

(2, 2) and Wassiljewa models also did well. The former performed best with mass fractions.

Tables 7 and 8 and Fig. 5 show the regression results for the ternary mixture of R32, R125, and R134a. As before, model parameters were obtained using only pure and binary mixture property data. The linear blending rule and the Vredeveld equation did very poorly independent of whether the mass or mole fraction was selected as the composition variable. The quadratic Scheffé model again performed surprisingly well. In this case, it performed better with mass fraction than with mole fractions. The Padé (2, 2) and Wassiljewa models did well too; the latter performed best with mole fractions.

4 Conclusion

The correlation of experimental thermal-conductivity data for pure heat transfer fluids and their ternary liquid mixtures was studied. The systems considered included the extensive isothermal data, for ternary organic liquid mixtures, reported by Rowley and

Table 7 Comparing thermal-conductivity mixture models for blends of R32, R125, and R134a (System V) [2–4,6–8,10,11]

Mixing rule	AAD (%) No. parameters	Mass basis Average	Mass basis Maximum	Mole basis Average	Mole basis Maximum
Linear blending rule	–	4.66	9.90	13.7	25.6
Vredeveld	–	5.53	16.29	2.99	8.67
Scheffé (2)[a]					
Binary	1	1.11	6.31	1.91	9.41
Ternary		1.95	4.57	2.62	5.62
Scheffé (2)[b]					
Binary	2	1.08	5.78	1.95	10.61
Ternary		1.97	4.88	2.61	5.58
Padé (2, 2)[a]					
Binary	2	1.10	6.68	1.08	5.37
Ternary		1.91	4.54	1.94	5.03
Wassiljewa					
Binary	2	1.15	5.90	1.08	5.94
Ternary		2.18	5.1	1.91	4.82

Ternary data predicted from model parameter fit using binary data where applicable

[a] Geometric combining rule (Eq. 34)

[b] Combining rule of Eq. 36

Table 8 Selected thermal-conductivity mixture model parameters for the system of R32 [3,4], R125 [6,10], and R134a [3,10]

	a_{12}	a_{13}	a_{23}			
Scheffé mass basis (Geometric combining rule)	0.9509	0.9226	1.0130			
	a_{12}	a_{13}	a_{23}	b_{12}	b_{13}	b_{23}
Padé (2, 2) mass basis	0.9045	0.9215	1.0084	0.9542	0.9989	0.9954
	α_{12}	α_{13}	α_{21}	α_{23}	α_{31}	α_{32}
Wassiljewa mole basis	0.4265	0.4643	1.7164	0.9494	1.7415	1.0146

coworkers [25,32,33]; the isobaric ternary liquid paraffin mixture reported by Wada et al. [1]; and the ternary refrigerant system based on R32, R125, and R134a [2,4,6, 10,11]. It was found that the combined temperature (T) and pressure (P) dependence for pure refrigerants is adequately described by low-order Chisholm approximants. These are rational functions based on truncated Taylor expansions in the two variables of temperature and pressure. For most refrigerants investigated here, the Chisholm (1, 1) approximant proved adequate. It is simply the ratio of two linear equations in T and P and has five adjustable parameters. Maximum and absolute average deviations (AAD's) between experimental and predicted values were less than 2.5 % and 1 %, respectively.

The observed isothermal-isobaric thermal-conductivity composition dependence did not deviate much from the linear blending rule. If mass fractions are used as the composition variable, the maximum deviations from the linear blending rule were less than 10 % for the data of Rowley et al. [25]. The fully predictive Vredeveld cor-

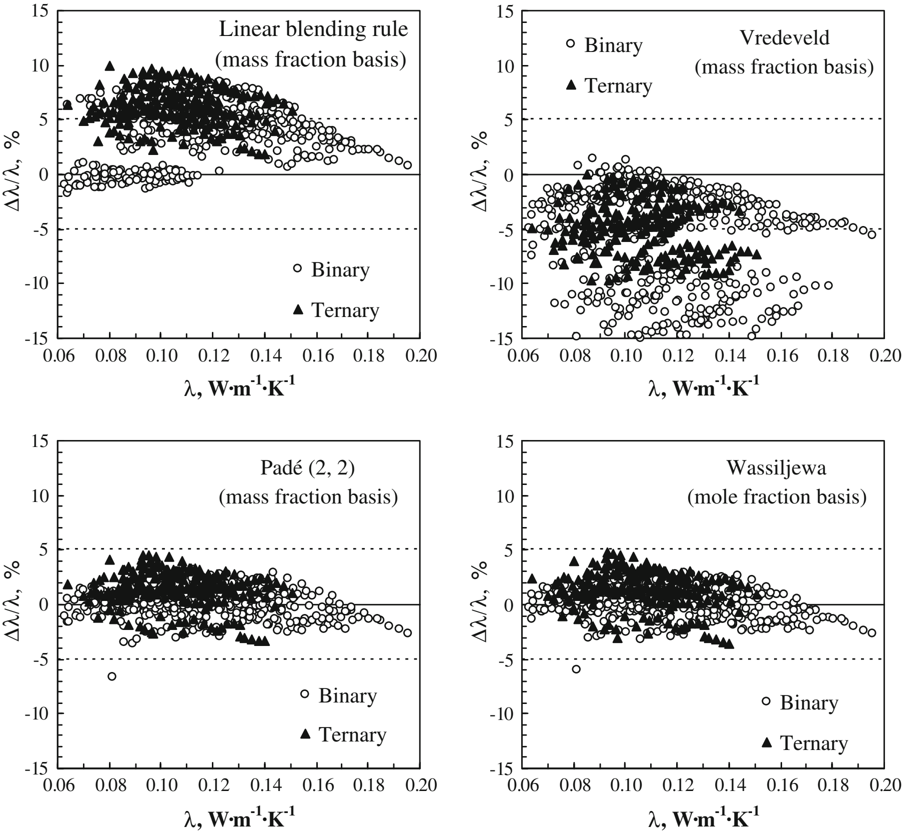

Fig. 5 Performance of the Vredeveld and Wassiljewa models for correlating the thermal-conductivity data for the ternary refrigerant mixture of R32, R125, and R134a [2–4,6,10,11]

relation is a mass fraction-weighted power mean of order −2 and is considered to be one of the better empirical models for liquid thermal conductivity [14]. For the present data, it proved inferior to the linear blending rule in some cases. The Padé (2, 2) model is a ratio of two quadratic Scheffé polynomials. Mixture composition effects were well represented using the quadratic Scheffé, the Padé (2, 2) approximant, or the Wassiljewa equation [30]. The latter two equations feature two adjustable binary cross parameters per binary instead of the single one for the quadratic Scheffé model. Two combining rules were considered. The simplest assumes that the binary cross parameters are proportional to the geometric mean of the pure-component thermal conductivities. The second is suggested by the theoretical Wassiljewa equation [30], first derived for the thermal conductivity of ideal-gas mixtures. When applied to the quadratic Scheffé polynomial, the number of adjustable parameters is increased to two per binary. With these proposals, the temperature dependence is fixed by the behavior of the pure components. These concepts were tested using the data for R32, R125, and R134a mixtures [2,4,6,10,11]. All three models predict ternary and higher mixture behavior from a knowledge of binary data. Therefore, only binary data were regressed to fix model parameters. The observed predictions for ternary compositions indicated the following: the Scheffé and Padé (2, 2) models work well when mass fractions are used whereas the Wassiljewa model fares better with mole fractions as the composition variable. Compared to previous suggestions [3–5,7,10], these models feature far fewer adjustable parameters yet provide acceptable data correlation performance and predictions for ternary mixtures. Furthermore, the adjustable constants in the mixture rule were temperature- and pressure-independent. Thus, these models should in the future be considered for correlating new thermal-conductivity data for other multicomponent liquid mixtures.

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