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A THERMAL CONDUCTIVITY PREDICTION METHOD FOR REFRIGERANT MIXTURES IN THE LIQUID PHASE

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ABSTRACT

Thermal conductivity is an important transport property in understanding heat transfer characteristics. It can be evaluated either from experimental measurements or theoretical predictions. In the present study, a theoretical model is proposed for predicting the thermal conductivity of a refrigerant mixture. This method requires speed of sound information obtained theoretically for a liquid mixture and the Carnahan-Starling-DeSantis (CSD) equation of state. This approach is based on applying to mixtures an equation suggested by Bridgman for pure substances. The application to mixtures is accomplished by inserting a coefficient into the equation. In this paper, modifying coefficients for 3 refrigerant mixtures: R22/R12, R22/R114, R22/R152a, were presented for the temperature range of -40°C to 60°C. Predicted thermal conductivity results were also compared with values obtained by other methods. The approach presented here shows that the thermal conductivity of mixtures can be directly calculated from knowing their thermodynamic properties.

NOMENCLATURE

a: equation of state attraction parameter(between species i,j)
a_0, a_1, a_2: coefficients for equation (A2)
b: equation of state parameter
b_0, b_1, b_2: coefficients for equation (A3)
C: modified coefficients for equation (2)
f_{ij}: interaction parameter between species i and j
K: thermal conductivity
k: specific heat ratio, C_p/C_v
M: molecular weight
N: Avogadro's number
P: pressure
R: gas constant
T: temperature
V_s: speed of sound
V: molar volume
v: specific volume
W: mass fraction
X: molar fraction
y: $b/4V$

Superscripts

n: polynomial power

Greek

σ: Boltzmann's constant
ρ: density

Subscripts

c: critical properties
cm: critical properties for mixtures
i,j: component i,j
l: liquid phase
m: mixture
n: polynomial coefficients
T: at constant temperature condition
r: reduced properties
m: reduced properties for mixtures

INTRODUCTION

Thermal conductivity property data is necessary for understanding the heat transfer characteristics of a fluid. It can be determined from either experimental measurements or theoretical predictions. To date, only a few theoretical equations have been developed to predict the thermal conductivity of mixtures[1-3]. A complication that exists when dealing with mixture problems is that a mixing rule is needed for estimating accurate mixture properties. Unfortunately, one mixing rule cannot always be broadly suitable for every pair with reasonable accuracy. In addition, the mixing rule usually needs to be based on experimental data.

From a theoretical standpoint, thermal conductivity is a property which is related to energy transfer through the molecular lattice. Therefore, speed of sound has some relevance to thermal conductivity. The use of speed of sound has been well established for predicting the thermal conductivity of pure fluids. However, there are no reports in the literature of applying this method to fluid mixtures.

The purpose of this paper is to use a speed of sound method to predict the thermal conductivity of refrigerant mixtures. One such method in the literature, which has been used for pure substance, is an approach known as the Bridgman equations[4]. In this paper, it is proposed that the Bridgman equation be applied to thermal conductivity predictions of mixtures by introducing modified coefficients in the equation. Modified coefficients, which are functions of reduced temperature and the type of pure substance used in the mixture, were found for three refrigerant mixtures. This method also requires knowledge of thermodynamic properties, such as pressure-volume-temperature. Since the CSD equation of state has been reported to produce good accuracy for mixtures, the CSD equation of state was used to calculate both the thermodynamic properties and the speed of sound in liquid mixtures[5,6].

Unlike other methods, such as the Filippov method, the method presented herein calculates thermal conductivity of mixtures directly from their thermodynamic properties without knowing the thermal conductivity of the pure substances.

METHODS FOR THERMAL CONDUCTIVITY PREDICTION

Proposed Approach for Mixture Thermal Conductivity

A theoretical equation for the thermal conductivity of liquids was proposed by Bridgman in 1923 and later, modified by Powel et. al.[4]. The resulting equation, which has been used for pure substances, is

$$K = 2.8\left(\frac{N}{V}\right)^{2/3} \sigma V_s \tag{1}$$

where

N = Avogadro's number
V = molar volume
σ = the Boltzmann's constant
V_s = the speed of sound

It is proposed here that this equation can be used for mixtures if the equation is modified by a coefficient, C_m, which is unique for the type of pure substances used in the mixture. Hence, the thermal conductivity for mixtures can be expressed as:

$$K_{lm} = 2.8C_m\left(\frac{N}{V_m}\right)_m^{2/3} \sigma V_{sm} \tag{2}$$

Additional modifications required for the above equation because of the presence of the mixture are

$$V_m = M_m v_m \tag{3}$$

$$M_m = X_1 M_1 + X_2 M_2 \tag{4}$$

$$X_1 = \frac{M_2 W_1}{M_2 W_1 + M_1 W_2} \tag{5}$$

$$X_2 = 1 - X_1 \tag{6}$$

where

M_m = is molecular weight of the mixture
v_m = is specific volume of the mixture
X_i = molar fraction of component i
M_i = molecular weight of pure substance i
W_i = mass fraction of each component

To verify the method, modified coefficients, C_m, were assumed to be a function of reduced temperature and fitted by a polynomial function. Reduced temperature is defined as follows:

$$T_{rm} = \frac{T}{T_{cm}} \tag{7}$$

where

$$T_{cm} = X_1 T_{c1} + X_2 T_{c2} \tag{8}$$

Modified coefficients, therefore, are expressed as:

$$C_m = \sum_{0}^{n} C_n T_{rm}^{n} \tag{9}$$

The modified coefficients as a function of reduced temperature can be obtained for each refrigerant mixture pair by using experimental data. However, in the absence of experimental data (which is the case for nearly all refrigerant mixtures), it was necessary to use another prediction method, such as the Filippov method to generate thermal conductivity mixture data so that the modifying coefficients could be found.

Filippov Rule

It was noted earlier that in the absence of experimental data for mixtures, the Filippov rule was used herein to generate mixture thermal conductivity data for obtaining the modifying coefficients. The Filippov rule as proposed by Filippov et. al. for predicting the thermal conductivity of refrigerant mixtures[7], is given by

$$K_{lm} = W_1 K_{l1} + W_2 K_{l2} - 0.72 (K_{l1} - K_{l2}) W_1 W_2 \tag{10}$$

where K_{lm} is the mixture thermal conductivity, and K_{l1}, K_{l2} represents the thermal conductivity for pure component 1 and pure component 2, respectively. In addition, W_i is the mass fraction for component i. The components were so chosen that $K_{l1} > K_{l2}$. This equation has been reported in the open literature to be accurate to within ±5%[8].

RESULTS AND DISCUSSIONS

To illustrate the method proposed herein, three different mixtures were selected for evaluation. They are R22/R12, R22/R114, R22/R152a. The polynomial coefficients, C_n, used to calculate the modified coefficients, C_m, by using equation (9) are listed in Table 1 for a fourth power polynomial function over a temperature range of -40°C to 60°C.

Table 1. Modified Coefficients for 4th Power Polynomial

	C_0	C_1	C_2	C_3	C_4
R22/R12	54.999	-307.28	659.91	-628.90	225.89
R22/R114	15.864	-90.751	212.58	-219.88	86.630
R22/R152a	15.397	-84.625	190.63	-190.50	72.483

A plot of modified coefficients, C_m, as a function of T_{rm} for the three refrigerant mixtures is shown in Figure 1. The modified coefficients increase with reduced temperature, and they vary from 1.5 to 2.5.

By using the modified coefficients found above, equation(2) can be used to predict mixture thermal conductivity. Figure 2 through 4 show thermal conductivity as function of R22 composition and temperature for R22/R12, R22/R114, and R22/R152a mixtures, respectively, based on this approach. A comparison between current predictions, the Filippov method, and the Baroncini method[7] is shown in Figure 5 for R22/R152a mixtures at a temperature 0°C. The agreement is generally within about ±5%. The current predictions are compared in more detail with the Filippov correlation for all three mixtures in Figure 6 through 8. Again, the agreement is generally within about ±5%.

The advantage of the current method is that thermal conductivity of mixtures can be calculated directly from thermodynamic properties. Other methods, such as the Filippov and Baroncini models, need the thermal conductivity of each pure substance before the mixture thermal conductivity can be predicted.

In addition, because the current method calculates mixture thermal conductivity directly from thermodynamic properties, it can also be extended to multi-component mixtures that are made up of more than two components. Thermodynamic properties still can be obtained from CSD equation of state for multi-component mixtures[6]. However, modified coefficients should be obtained from experimental data or some other predictable models for multi-component mixtures.

CONCLUDING REMARKS

A method for predicting the thermal conductivity of liquid mixtures without needing to know the thermal conductivity of each pure substance is presented herein. Results were obtained for three refrigerant mixtures, R22/R12, R22/R114, and R22/R152a, and compared to the Filippov model for various R22 mass fractions over a temperature range of -40°C to 60°C. The agreement between the two methods was generally within ±5%. Further validation of the method proposed herein is needed, especially as experimental data for refrigerant mixtures is made available.

ACKNOWLEDGMENTS

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APPENDIX

Overview of The CSD Equation of State for Mixtures

The method proposed herein for predicting the thermal conductivity of mixture requires calculating the thermodynamic properties of the mixture. A modification of the Carnahan-Starling hard sphere fluid was first proposed by DeSantis, et al. in 1976. This equation is referred to as the CSD equation of state. The equation is given by

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)}, \quad y = b/4V \qquad \text{(A1)}$$

where

$$a = a_0 \exp(a_1 T + a_2 T^2) \qquad \text{(A2)}$$

$$b = b_0 + b_1 T + b_2 T^2 \qquad \text{(A3)}$$

This equation of state can be applied to either pure components or multi-component mixtures. If it is applied to mixtures, a mixing rule is required. In CSD modeling, the mixing rule is defined as follows:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} X_i X_j a_{ij} \qquad \text{(A4)}$$

$$b = \sum_{i=1}^{n} \sum_{j=1}^{n} X_i X_j b_{ij} \tag{A5}$$

where X_i , X_j are molar fraction. The values of a and b are the key to solving equation(A1) for mixture properties. The coefficients of a_{ij}, and b_{ij} can be obtained from experimental data. To determine a_{ij}, an interaction parameter, f_{ij}, is employed where the interaction parameter represents interaction forces between molecules. A relationship for f_{ij} and a_{ij} can be defined as follows:

$$a_{ij} = (1 - f_{ij})\,(a_{ii} \times a_{jj})^{1/2} \tag{A6}$$

b_{ij} was simplified to the average value of b_{ii} and b_{jj}

$$b_{ij} = 0.5(b_{ii} + b_{jj}) \tag{A7}$$

Overview of Speed of Sound for Mixtures

Theoretical speed of sound in the liquid phase of a pure substance is defined as:

$$V_s = \left[\, k \left(\frac{\partial P}{\partial \rho}\right)_T \right]^{1/2} \tag{A8}$$

where
$k = C_p/C_v$

The application of this equation can be extended to mixtures, if mixture properties are known. Therefore,

$$V_{sm} = \left[\, k \left(\frac{\partial P}{\partial \rho}\right)_T \right]_m^{1/2} \tag{A9}$$

where C_p, C_v, P and V are mixture properties which can be found from the CSD equation of state. Specifically, taking the first derivative of P with respect to ρ from the CSD equation of state, we obtain

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{RT}{M(V - b/4)^4}\left(V^4 + bV^3 + \frac{1}{4}b^2V^2 - \frac{1}{16}b^3V + \frac{1}{256}b^4\right) - \frac{a(2V + b)}{M(V + b)^2} \tag{A10}$$

Finally, the speed of sound equation for mixtures can be rearranged to obtain:

$$V_{sm} = \left[\frac{kRT}{M_m(V - b/4)^4}\left(V^4 + bV^3 + \frac{1}{4}b^2V^2 - \frac{1}{16}b^3V + \frac{1}{256}b^4\right) - \frac{ka(2V + b)}{M_m(V + b)^2}\right]^{1/2} \tag{A11}$$

Fig. 1. Thermal Conductivity Modified Coefficients

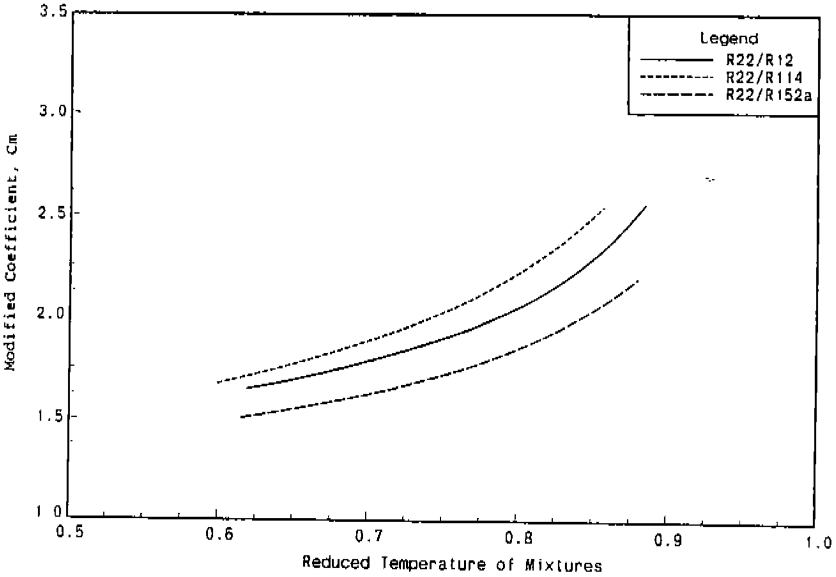


Fig. 2. Thermal Conductivity Prediction for R22/R12 Mixture

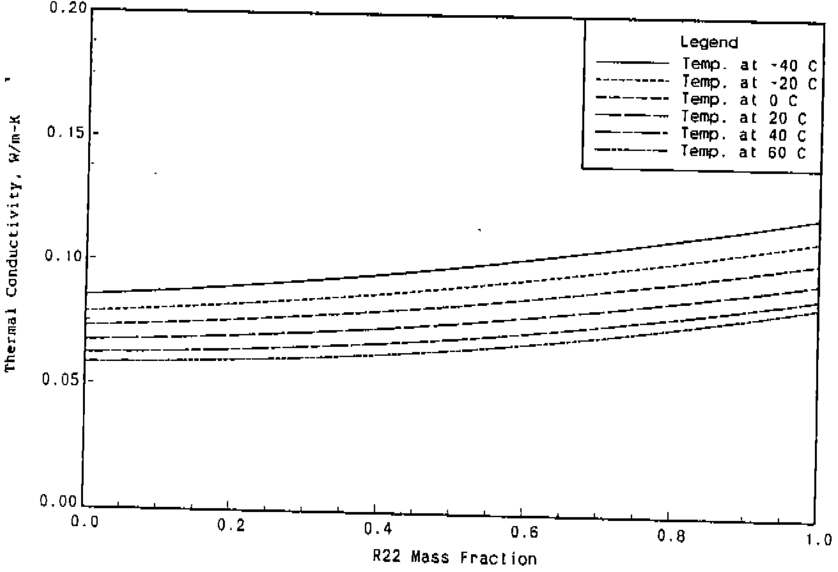


Fig. 3. Thermal Conductivity Prediction for R22/R114 Mixture

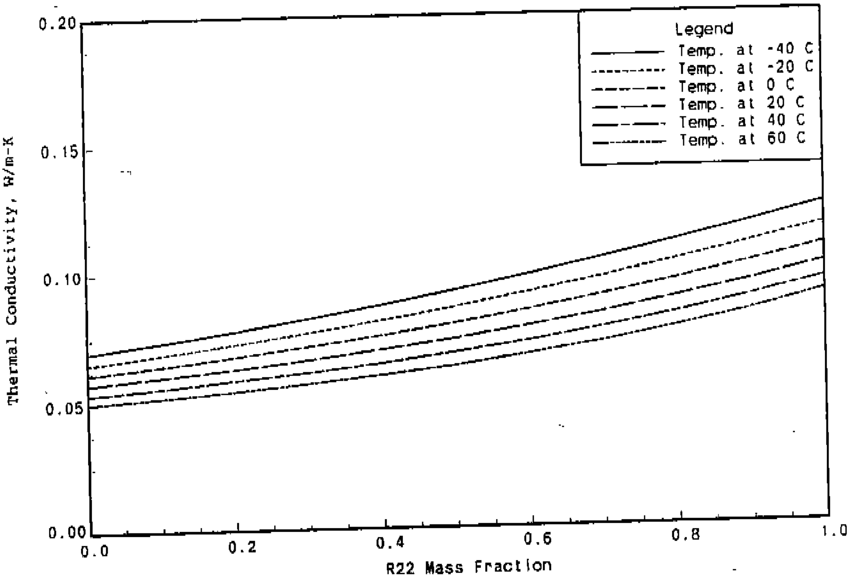


Fig. 4. Thermal Conductivity Prediction for R22/R152a Mixture

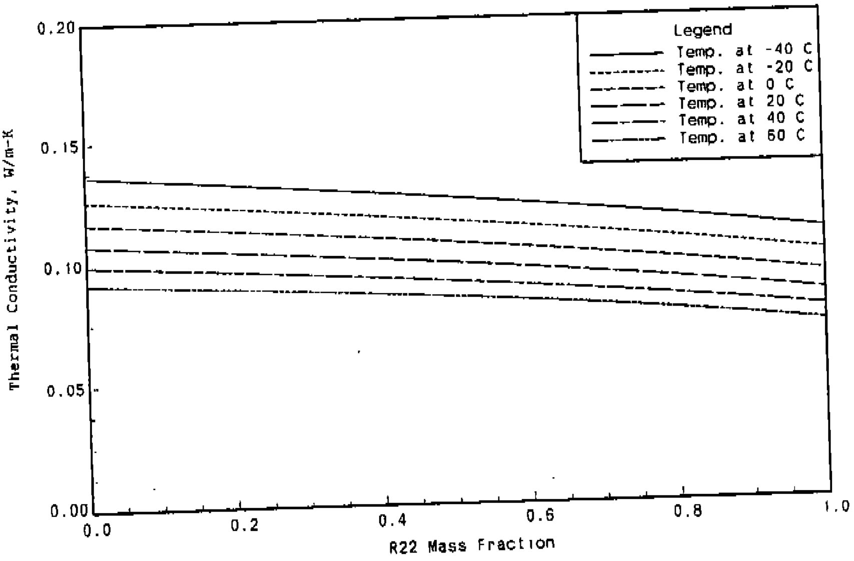


Fig. 5. Thermal Conductivity of R22/R152a Mixture at 0 C

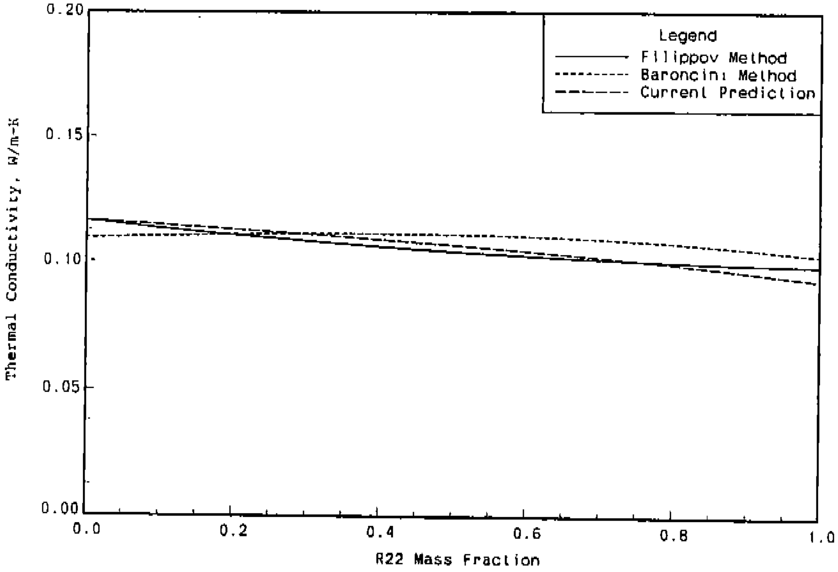


Fig. 6. Thermal Conductivity Prediction for R22/R12 Mixture

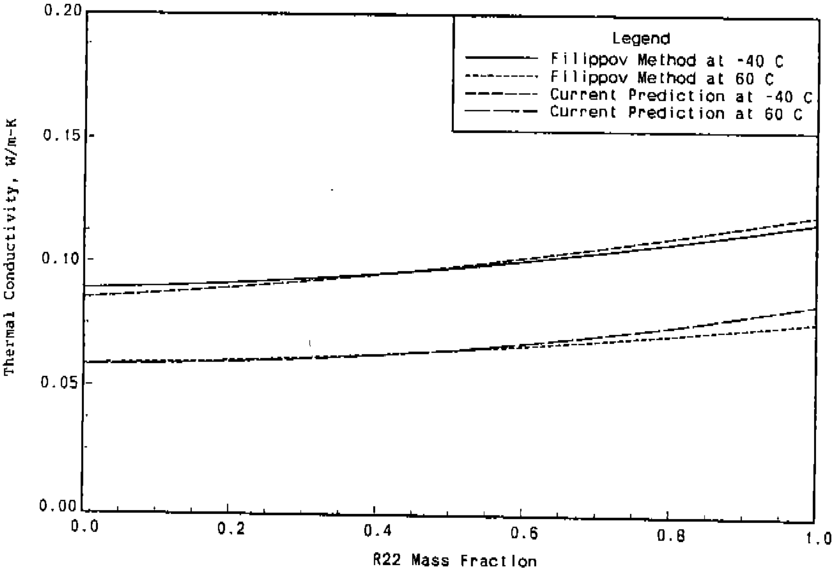
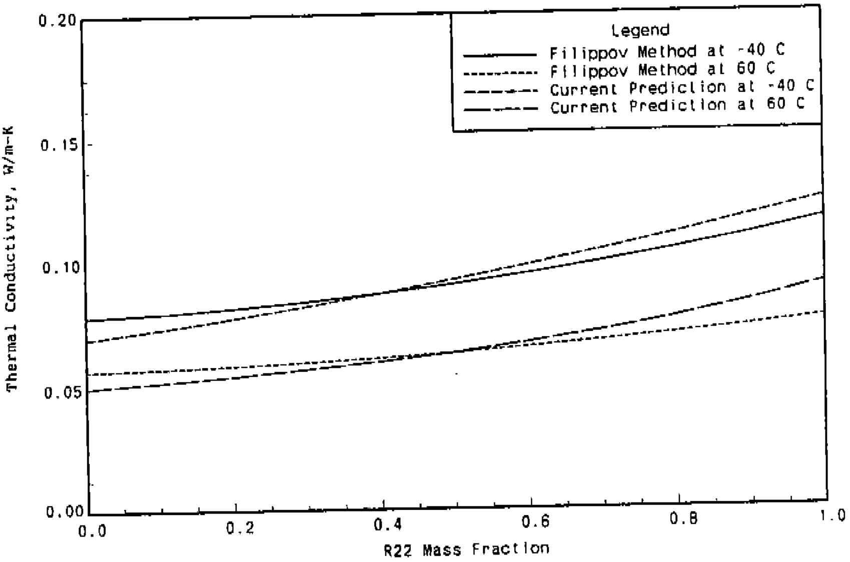


Fig. 7. Thermal Conductivity Prediction for R22/R114 Mixture



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