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Prediction of the Thermal Conductivity and Viscosity of Binary and Ternary HFC Refrigerant Mixtures

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A recently developed scheme, based on considerations of hard-sphere theory, is used for the simultaneous prediction of the thermal conductivity and the viscosity of binary and ternary HFC refrigerant mixtures, consisting of HFC-32, HFC-125, and HFC-134a. In this prediction scheme, the hypothetical molecular parameters of HFC refrigerant mixtures were assumed to be the molar average of the pure component values. The close agreement between the predicted values and the experimental results of thermal conductivity and viscosity demonstrate the predictive power of this scheme.

KEY WORDS: HFC-32; HFC-125; HFC-134a; hard-sphere theory; mixture; refrigerant; thermal conductivity; viscosity.

1. INTRODUCTION

HFC refrigerant mixtures will have extensive application as HCFC refrigerants are gradually phased out. Thus, accurate thermal conductivity and viscosity data are required for HFC refrigerant mixtures when designing new refrigeration systems. Compared with research on thermodynamic properties, data for transport properties of HFC refrigerant mixtures are very scarce at present. It is not possible to measure the transport properties of all relevant mixture compositions. Hence, prediction methods, based on rigorous theory, become more and more important in the evaluation of transport properties of HFC refrigerant mixtures.

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There are several recommended methods for predicting the transport properties of liquid mixtures [1]. The Grünberg–Nissan equation or the Teja–Rice relation is often applied to estimate and to predict the viscosity of liquid mixtures. In the case of prediction of the thermal conductivity of liquid mixtures, the Filippov equation, the Jamieson correlation, the Baroncini correlation, the correlation of Rowley, and the Li method are often used in engineering applications. However, most of them lack a rigorous theoretical basis and need adjustable parameters which must be determined from experimental data. One of the most widely employed schemes today is based on the corresponding-states approach. Although this approach also lacks a rigorous theoretical approach and shape factors are employed to get better agreement with experimental results, commercial computer packages based on this approach are usually very good. However, the situation becomes worse the higher the degree of complexity of molecular structure or the degree of polarity. Therefore, the development of new reliable prediction methods based on rigorous theory is important for the estimation and prediction of transport properties of liquid mixtures.

Recently, a semiempirical scheme based on considerations of the hard-sphere theory was developed for the correlation and prediction of the transport properties of liquids. The work of Assael and Dymond [2–5] showed that the rough hard-sphere scheme provided a good correlation basis of the transport properties of liquid *n*-alkanes, aromatic hydrocarbons, alcohols, and refrigerants. This method was also shown to be effective for the prediction of the transport properties of *n*-alkane mixtures [6] using the mole fraction mixing rules to calculate the mixture molecular parameters. Until now, however, the scheme has not been tested against other than *n*-alkane mixtures. This was mostly attributed to a lack of accurate measurements over a wide range of conditions. The extension of this scheme to the prediction of the thermal conductivity and viscosity of HFC refrigerant mixtures is reported here.

2. ROUGH HARD-SPHERE THEORY

According to the proposed scheme [2], it was found that the reduced coefficients for viscosity and thermal conductivity of pure fluids, defined as

$$\eta^* = 6.035 \times 10^8 \times \left(\frac{1}{MRT}\right)^{1/2} \eta V^{2/3} \tag{1}$$

$$\lambda^* = 1.936 \times 10^7 \times \left(\frac{M}{RT}\right)^{1/2} \lambda V^{2/3} \tag{2}$$

Table I. Coefficients $a_{\eta i}$ and $a_{\lambda i}$ in Eqs. (3) and (4), Respectively

i	$a_{\eta i}$	$a_{\lambda i}$
0	1.0945	1.0655
1	−9.26324	−3.538
2	71.0385	12.120
3	−301.9012	−12.469
4	797.6900	4.562
5	−1221.9770	—
6	987.5574	—
7	−319.4636	—

are functions only of the reduced molar volume $V_r = (V/V_o)$, where V_o is a characteristic molar volume of the liquid, weakly temperature dependent. In the above equations, M is the molar mass, T is the absolute temperature, R is the universal gas constant, V is the molar volume, and all quantities are expressed in SI units. The aforementioned functions were found to be universal for all liquids and equal to

$$\log\left(\frac{\eta^*}{R_\eta}\right) = \sum_{i=0}^{7} a_{\eta i}\left(\frac{V}{V_0}\right)^{-i} \tag{3}$$

$$\log\left(\frac{\lambda^*}{R_\lambda}\right) = \sum_{i=0}^{4} a_{\lambda i}\left(\frac{V}{V_0}\right)^{-i} \tag{4}$$

where constants $a_{\eta i}$ and $a_{\lambda i}$ are given in Table I. The parameters R_η and R_λ, called roughness factors, account for deviations from the behavior of smooth hard spheres [2]. In the case of the alkanes the roughness factors were found to be constant, while in the case of the alcohols or the refrigerants, they were sometimes found to be weakly temperature dependent.

Accurate thermal conductivity and viscosity measurements can be employed to calculate the roughness factors and the characteristic molar volume of each fluid. It should also be pointed out that since the characteristic molar volume is only weakly temperature dependent, atmospheric pressure measurements can be employed for its calculation and thus high-pressure values can be predicted.

2.1. Pure Fluids

The aforementioned scheme was successfully employed for the correlation of the liquid refrigerants [4]. However, its use at low temperatures was hindered by a lack of measurements in that region.

To determine the characteristic molar volume V_o and the roughness factors R_η and R_λ for HFC-32, HFC-125, and HFC-134a, the thermal conductivity data reported in our previous work [7–9] were used. As for viscosity data, the data for HFC-32 measured by Assael et al. [10], Oliveira and Wakeham [11], and Ripple and Matar [12] were used. In the case of HFC-125 the data employed were from Assael and Polimatidou [13], Diller and Peterson [14], and Ripple and Matar [12], while for HFC-134a the data measured by Assael et al. [10], Oliveira and Wakeham [15], and Okubo et al. [16] were used. The international standard equation of state for HFC-32 developed by Tillner-Roth and Yokoseki [17], the equation of state for HFC-125 developed by Outcalt and McLinden [18], and the international standard equation of state for HFC-134a developed by Tillner-Roth and Baehr [19] were employed to calculate the density in the liquid phase.

The characteristic molar volume V_o and the roughness factor for the thermal conductivity R_λ for HFC-32, HFC-125, and HFC-134a were correlated by a polynomial in the reduced temperature $T_r = T/T_c$, as

$$10^6 \times V_0 = \sum_{i=1}^{4} e_i T_r^{i-1} \tag{5}$$

$$R_\lambda = \sum_{i=1}^{4} h_i T_r^{i-1} \tag{6}$$

The coefficients e_i and h_i of these equations are listed in Tables II and III. The roughness factors for viscosity R_η were found to be temperature independent, and their values are listed in Table IV. Plots of the characteristic molar volume and the roughness factors for the thermal conductivity for the three refrigerants studied are presented in Figs. 1 and 2.

Equations (1) to (6) form a consistent set for correlating the thermal conductivity and viscosity of these refrigerants. The scheme was found to

Table II. Coefficients e_i in Eq. (5)

	HFC-32	HFC-125	HFC-134a
Molecular mass ($g \cdot mol^{-1}$)	52.02	120.02	102.03
Critical temperature (K)	351.26	339.33	374.21
e_1	53.419159	40.274131	49.758588
e_2	−107.67454	32.238131	−9.0398452
e_3	134.32831	−38.738375	7.1777544
e_4	−60.713021	5.9901023	−7.2956217

Table III. Coefficients h_i in Eq. (6)

	HFC-32	HFC-125	HFC-134a
h_1	-2.6882029	3.8986304	1.1659317
h_2	16.580611	-7.4685792	1.7780147
h_3	-21.540006	7.1328808	-3.4044416
h_4	9.9257518	-1.3387434	2.364606

Table IV. Roughness Factors for Viscosity

	HFC-32	HFC-125	HFC-134a
R_η	1.2239	1.4073	1.0997

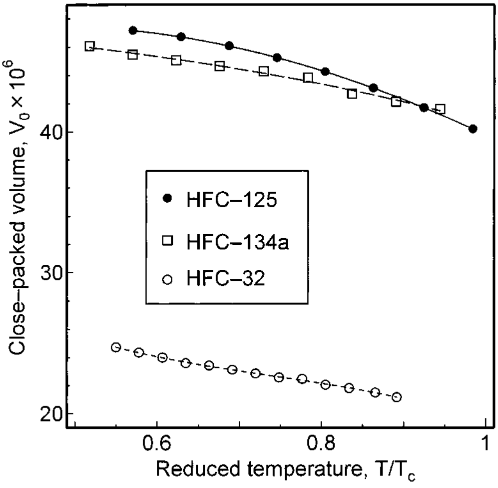

Fig. 1. Temperature dependence of the obtained close-packed volumes for HFC-32, HFC-125, and HFC-134a in the liquid phase.

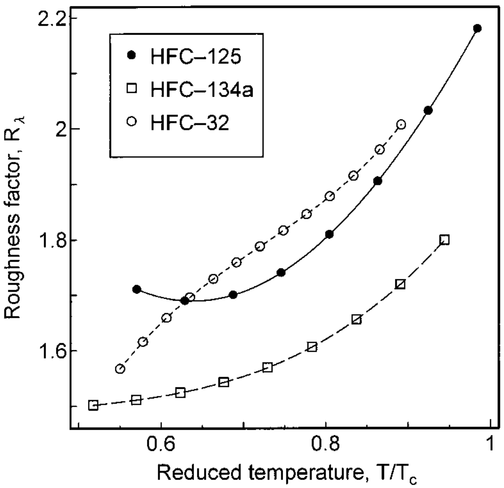

Fig. 2. Temperature dependence of the obtained roughness factors of HFC-32, HFC-125, and HFC-134a for thermal conductivity in the liquid phase.

represent the thermal conductivity data for HFC-32, HFC-125, and HFC-134a with standard deviations of 1.5, 1.5, and 2.3%, respectively, and the viscosity data for HFC-32, HFC-125, and HFC-134a with standard deviations of 1.5, 5.1, and 1.7%, respectively.

2.2. Mixtures

Prediction of the thermal conductivity and viscosity of liquid mixtures based on the scheme as applied to *n*-alkane mixtures [6] assumed that the mixture behaves as a hypothetical pure liquid with molecular parameters given by the mole fraction average of the pure component values, i.e.,

$$V_{0,\,\mathrm{mix}} = \sum_{i=1}^{i} x_i V_{0,\,i}, \qquad R_{\lambda,\,\mathrm{mix}} = \sum_{i=1}^{i} x_i R_{\lambda,\,i}, \qquad R_{\eta,\,\mathrm{mix}} = \sum_{i=1}^{i} x_i R_{\eta,\,i} \tag{7}$$

where x_i are the mole fractions of the pure components, and the subscripts i and mix denote the pure components and the mixture, respectively. The mixture density employed was also calculated by the mole fraction average of the pure component densities. No parameter of the mixtures was employed and as such, the scheme is a clearly predictive scheme.

The liquid thermal conductivity of the binary mixtures, HFC-32/HFC-125 and HFC-32/HFC-134a, and two ternary mixtures of HFC-32/HFC-125/HFC-134a (R-407C: 23/25/52 wt% and 33.4/33.3/33.3 mol%), which

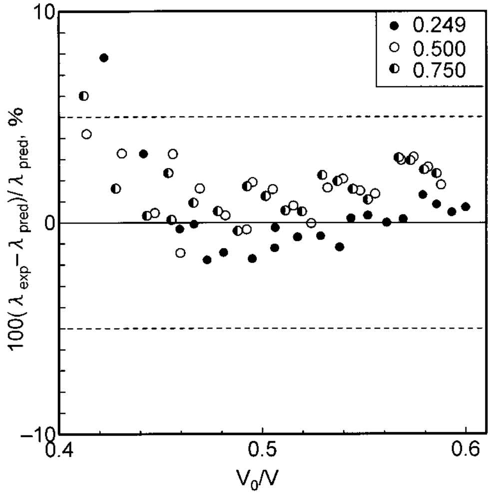

Fig. 3. Percentage deviations of the experimental results of liquid thermal conductivity from the predicted values for mixtures of HFC-32/HFC-125.

have been reported [20, 21], were employed to check the predictive power of this scheme. Figure 3 shows the percentage deviations of the experimental thermal conductivity data from the predicted values for mixtures of HFC-32/HFC-125. Only two points show deviations of more than 5 % from the experimental values, while all other data agree very well with experimental results. The standard and maximum deviations between the predicted values and the experimental results are 2.1 and −7.8 %, respectively.

Figure 4 illustrates the percentage deviations of the experimental results from predicted values for the mixture HFC-32/HFC-134a. Only four points deviate more than 5.0 %. The predicted values agree with the experimental results with a standard deviation of 2.3 % and maximum deviation of −6.9 %.

Figure 5 shows the percentage deviations between the experimental results of thermal conductivity and the predicted values for ternary mixtures of HFC-32/HFC-125/HFC-134a (R-407C: 23/25/52 wt % and 33.4/33.3/33.3 mol %). The present experimental results are a little lower than the predicted values, although the largest deviation does not exceed −5.7 %. The standard and the maximum deviations of the experimental results from the predicted values are 2.9 and −5.7 %, respectively.

The good agreement of the predicted values with the experimental results of thermal conductivity for the mixtures HFC-32/HFC-125, HFC-32/134a, and HFC-32/HFC-125/HFC-134a showed that the prediction

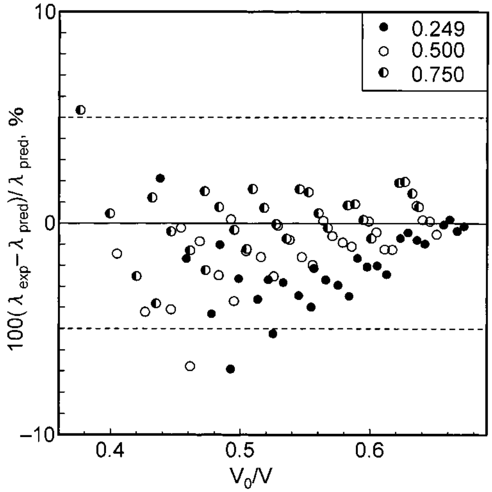

Fig. 4. Percentage deviations of the experimental results of liquid thermal conductivity from the predicted values for mixtures of HFC-32/HFC-134a.

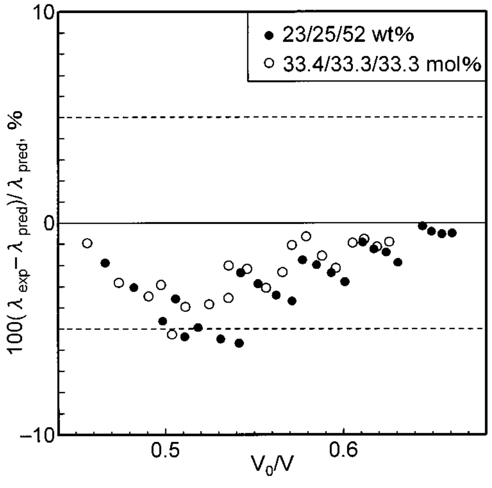

Fig. 5. Percentage deviations of the experimental results of liquid thermal conductivity from the predicted values for mixtures of HFC-32/HFC-125/HFC-134a.

scheme based on the hard-sphere theory is effective in predicting the thermal conductivity of HFC refrigerant mixtures.

Measurements of the saturated liquid viscosity for the mixtures HFC-32/HFC-134a and HFC-125/HFC-134a were reported by Ripple and Matar [12]. Values for the binary mixtures were calculated and compared with the experimental results of Ripple and Matar. Figure 6 shows the percentage deviations of the experimental results of Ripple and Matar for mixtures of HFC-32/HFC-134a from the predicted values. Although the experimental results are a little larger than the present predicted values, the agreement is satisfactory. The standard deviation and the maximum deviation between the predicted and the experimental results are 1.9 and 3.9%, respectively. Figure 7 shows the percentage deviations of the experimental results of Ripple and Matar [12] for the mixtures of HFC-125/HFC-134a compared with the predicted values. The predicted viscosity results for the mixtures of HFC-125/HFC-134a agree with the experimental results with a standard deviation of 1.5% and a maximum deviation of 3.5%.

Through these comparisons of the predicted values and the experimental results of viscosity for the mixtures HFC-32/HFC-134a and HFC-125/134a, the scheme based on the hard-sphere theory is shown to be effective in predicting the liquid viscosity of HFC refrigerant mixtures.

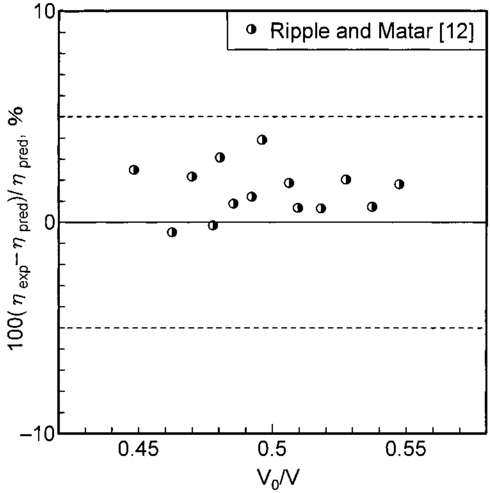

Fig. 6. Percentage deviations of the experimental results of Ripple and Matar for the saturated liquid viscosity from the predicted values for mixtures of HFC-32/HFC-134a.

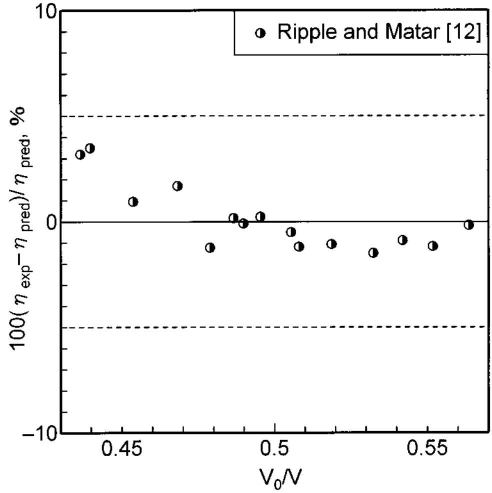

Fig. 7. Percentage deviations of the experimental results of Ripple and Matar for the saturated liquid viscosity from the predicted values for mixtures of HFC-125/HFC-134a.

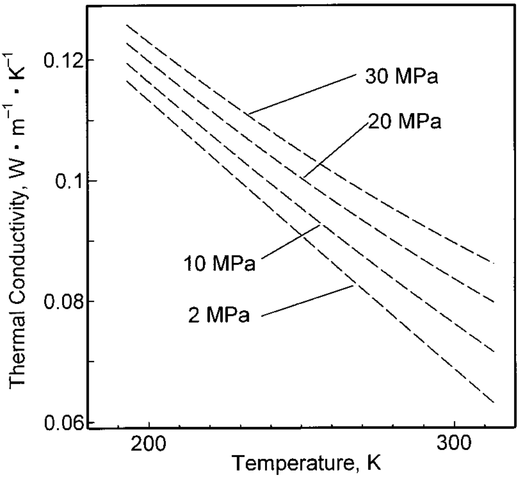

Fig. 8. Temperature dependence of the predicted values of thermal conductivity for the mixture of HFC-125/HFC-134a (mass fraction of HFC-125: 0.500).

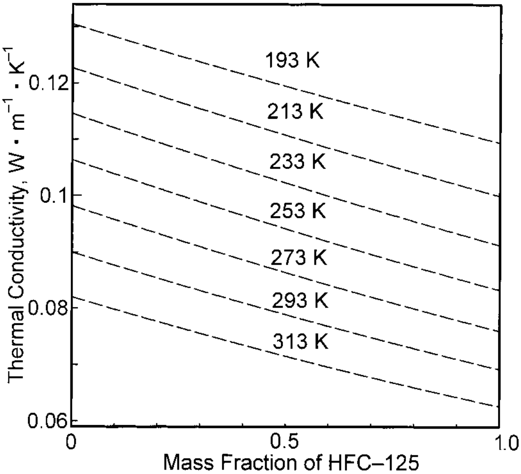

Fig. 9. Mass fraction dependence of the predicted values of thermal conductivity for the mixture of HFC-125/HFC-134a (mass fraction of HFC-125: 0.500).

Making use of the above-mentioned prediction scheme, the liquid thermal conductivity of binary HFC refrigerant mixtures of HFC-125/HFC-134a and ternary mixtures of HFC-32/HFC-125/HFC-134a (R-407A, R-407B, R-407D, R-407E), which were not measured in the present study, was predicted in the temperature range from 193 to 313 K and in the pressure range from 2 to 30 MPa. Figure 8 shows the temperature dependence of the predicted thermal conductivity data for the mixture HFC-125/HFC-134a with a mass fraction of HFC-125 equal to 0.50. Figure 9 shows the mass fraction dependence of the predicted values of thermal conductivity for the same mixtures at 10 MPa.

3. CONCLUSIONS

The thermal conductivity and viscosity of HFC mixtures consisting of HFC-32, HFC-125, and HFC-134a were successfully predicted with the hard-sphere scheme employed here over a wide range of conditions. Only properties of the pure components were employed and the mixture parameters were assumed to be mole fraction averages of the pure component values. It is indeed most encouraging that the one-fluid approach, with these simple combining rules, gives such a satisfactory prediction of the mixture transport properties for these refrigerants. It will be interested to examine the prediction of these properties for more mixtures.

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