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PREDICTION OF THE THERMAL CONDUCTIVITY OF CIS-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE (R-1336MZZ(Z)) THROUGH EXTENDED CORRESPONDING STATES MODEL

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Abstract- *A Hydro-Fluoro-Olefin (HFO) cis-1,1,1,4,4,4-hexafluoro-2-butene (R-1336mzz(Z)) is considered as a potential replacement of Hydrofluorocarbons (HFCs) due to environmental concern over global warming. In this work, the extended corresponding states (ECS) models coupled with density-independent shape factors (empirical shape factors) or density-dependent shape factors (exact shape factors) are individually applied to predict the thermal conductivity of R-1336mzz(Z). These models use 1,1,1,2-Tetrafluoroethane (R-134a) as a reference fluid. Empirical shape factors are obtained from the vapor pressures and saturated liquid densities of R-1336mzz(Z) and R-134a. Exact shape factors are calculated from equations of state for these refrigerants. Predctied values with the ECS models are compared with experimental data, and the prediction capability of each model is discussed. In addition, thermal conductivity shape factor is introduced to improve the prediction capability. With these additional shape factors, the ECS models represent the experimental data of the thermal conductivity of R-1336mzz(Z) within ±2%.*

Keywords: Thermal Conductivity, Extended Corresponding States Model, Empirical Shape Factor, Exact Shape Factor, R-1336mzz(Z)

1. INTRODUCTION

Hydrofluorocarbons (HFCs) are commonly used a refrigerant in refrigeration and air-conditioning system. In the Kigali Amendment of the Montreal Protocol [1], all nations in the world committed to significantly reduce the consumption and production of HFCs as they have high Global Warming Potential (GWP). Several alternatives are searched to replace the HFCs in the refrigeration system. A Hydro-Fluoro-Olefin (HFO) cis-1,1,1,4,4,4-hexafluoro-2-butene (R-1336mzz(Z)) is considered as a potential working fluid for various applications including air conditioning chillers [2], high temperature heat pumps [3], and Organic Rankine Cycles (ORC) [4] because of its very low GWP, nonflammability, thermal stability, low toxicity and attractive thermodynamic properties. The ozone depletion potential (ODP) of R-1336mzz(Z) is zero, and the GWP is 2 [5], the atmospheric lifetime is approximately 22 days [6] and it is a non-flammable and low toxic refrigerant [6].

Prediction of the thermal conductivity of R-1336mzz(Z) is a very important to implement it in practical system. Alam et al. [7] measured the thermal conductivity of this fluid by using Transient Hot Wire method and provided simplified correlations for saturated liquid and vapor. In this work, the thermal conductivity of R-1336mzz(Z) is predicted using a well-known extended corresponding states (ECS) model and compared with experimental values.

2. PREDICTION OF THE THERMAL CONDUCTIVITY

The thermal conductivity λ [W m-1 K-1] of R-1336mzz(Z) is expressed as a sum of four contributions as follows:

$$\lambda(\rho,T) = \lambda^{\mathrm{int}}(T) + \lambda^{*}(T) + \Delta\lambda_{\mathrm{r}}(\rho,T) + \Delta\lambda_{\mathrm{c}}(\rho,T) \quad (1)$$

where λ^{int} is the internal contribution, λ^{*} is the dilute-gas thermal conductivity depending only on temperature, $\Delta\lambda_{\mathrm{r}}$ is the residual thermal conductivity, and $\Delta\lambda_{\mathrm{c}}$ is the enhancement of the thermal conductivity in the critical region.

The internal contribution and dilute-gas thermal conductivity, which are the function of only temperature, are calculated from the equations (2) and (3) respectively.

$$\lambda^{\text{int}}(T) = f_{\text{int}}\eta^*(T)\left[c_P^{\circ}(T) - \frac{5}{2}R\right] \quad (2)$$

$$\lambda^*(T) = \frac{15}{4}R\eta^*(T) \quad (3)$$

$$\eta^*(T) = \frac{5}{16\sigma^2\Omega^{(2,2)}}\sqrt{\frac{Mk_BT}{\pi N_A}} \quad (4)$$

where c_P° is the ideal-gas isobaric heat capacity [J mol^{-1} K^{-1}], R is the universal gas constant [8.314472 J mol^{-1} K^{-1}], and f_{int} is a factor that accounts for the energy conversion between internal and translational modes. A value of f_{int} is set to 1.32 according to the formulation by Huber et al. [8]. η^* is the dilute-gas viscosity and calculated by the Chapman and Enskog theory.

The last two contributions are the functions of temperature and density. The residual thermal conductivity $\Delta\lambda_r$ is calculated from the ECS model. The critical enhancement $\Delta\lambda_c$ is calculated from the simplified crossover model developed by Olchowy and Sengers [9].

The concept of ECS model is based on the corresponding states principle between a fluid of interest and a reference fluid. It was originally proposed by Leland and Chappelear [10], and after that several modifications have been made to apply this model to various fluids. NIST (National Institute of Standards and Technology, USA) has been extensively used the model for the calculations of transport properties [8,11,12] and these calculations are currently available on their property calculation software REFPROP 9.1 [13]. Akasaka [14] used this model for prediction of the viscosity of 2,3,3,3-tetrafluoropropene (R1234yf). Islam et al. [15] also used this method for prediction of the viscosity and thermal conductivity of 1,3,3,3-tetrafluoropropene (R1234ze(Z)). Similar procedures are applied in this work to predict the thermal conductivity of R1336mzz(Z). The temperature and density of R1336mzz(Z) (T and ρ) are linked with conformal values of the reference fluid R134a (T_0 and ρ_0) according to the relations given below:

$$T_0 = \frac{T}{f} \quad (5)$$

$$\rho_0 = \rho h \quad (6)$$

where f and h are equivalent substance reducing ratios. They are defined as

$$f = \frac{T_c}{T_{c,0}}\theta(T,\rho) \quad (7)$$

$$h = \frac{\rho_{c,0}}{\rho_c}\phi(T,\rho) \quad (8)$$

The parameters θ and ϕ are called the shape factors. The subscript c indicates critical parameters given in Table 1.

Table 1. Critical parameters and acentric factors of R134a and R1336mzz(Z)

Properties	R134a*	R1336mzz(Z)
Molecular Weight (g.mol-1)	102.03	164.056
Critical temperature (K)	374.21	444.42**
Critical pressure (MPa)	4.0593	2.901**
Critical Density (mol.dm-3)	5.0171	2.934**
Acentric factor	0.32684	0.3853**
*All properties of R134a listed here come from REFPROP [13]		
** Akasaka and Lemmon [16]		

2.1 Empirical Shape Factor

Empirical shape factors are density independent parameters derived from properties at the saturation state. The equivalent substance reducing ratios, f and h, are obtained by solving the Eqs. (9) and (10) [11].

$$P^{sat}(T) = P_0^{sat}\left(\frac{T}{f}\right)\frac{f}{h} \quad (9)$$

$$\rho^{sat}(T) = \frac{\rho_0^{sat}\left(\frac{T}{f}\right)}{h} \quad (10)$$

where P^{sat} and P_0^{sat} are the vapor pressures of R1336mzz(Z) and R134a, respectively, and ρ^{sat} and ρ_0^{sat} are the saturated liquid densities of R1336mzz(Z) and R134a, respectively. For correlations for the shape factors in Eqs. (7) and (8), this work uses following equations:

$$\theta(T) = 1 + (\omega - \omega_0)(k_1 + k_2 \ln T_r + k_3 T_r) \quad (11)$$

$$\phi(T) = \frac{Z_{c,0}}{Z_c}\left[1 + (\omega - \omega_0)(l_1 + l_2 \ln T_r + l_3 T_r)\right] \quad (12)$$

where T_r is the reduced temperature ($T_r = T/T_c$), ω is the acentric factor, Z_c is the critical compressibility factor. Subscript 0 denotes the values for reference fluid R134a.

First f and h are obtained from Eqs. (9) and Eq. (10). The vapor pressures and saturated liquid densties of R134a (P_0^{sat} and ρ_0^{sat}) are calculated from the equation of state by Tillner-Roth and Baehr [17], and those of R1336mzzze(Z) (P^{sat} and ρ^{sat}) are calculated from the equation of state by Akasaka and Lemmon [16]. Subsequently, θ and ϕ are calculated from Eqs.(7) and (8). Calculated values of θ and ϕ are graphically shown in Fig 1. Finally, coefficients k_1, k_2, k_3, l_1, l_2, and l_3 are determined by fitting these θ and ϕ values to the equations given by Eqs. (11) and (12). Final values of the coefficients are given in Table 2.

2.2 Exact Shape Factor

Exact shape factors are density dependent parameters calculated from equations of state for fluid of interest and reference fluid. Conformal temperature and density are defined by equating the reduced Helmholtz energies and compressibility factors of both fluids. These equalities are expressed by Eqs. (13) and (14).

$$\alpha^{\mathrm{r}}(T,\rho) = \alpha_0^{\mathrm{r}}(T_0,\rho_0) \tag{13}$$

$$Z(T,\rho) = Z_0(T_0,\rho_0). \tag{14}$$

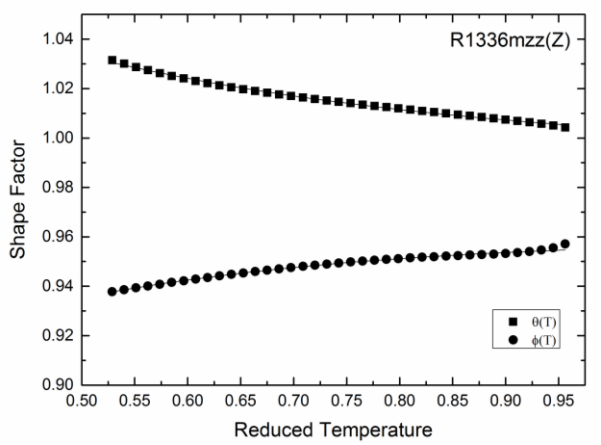

Fig. 1: Variation in empirical shape factors with reduced temperature

Table 2. Coefficients k_i and l_i in Eqs. (11) and (12)

i	k_i	l_i
1	247.4643	-897.9464
2	195.1071	-571.375
3	-236.4821	833.5

Solving of the simultaneous equations given by Eqs. (13) and (14) requires accurate equations of state over the entire fluid region. This work uses the equation of state by Akasaka and Lemmon [16] for α_r and Z, and employs the equation by Tillner-Roth and Baehr [17] for α_0^{r} and Z_0. The Newton-Rapson method is used as the root finding algorithm.

2.3 Residual components of the thermal conductivity

The residual components of the thermal conductivity in Eq (1) are calculated from the following equations:

$$\Delta\lambda^{\mathrm{r}}(T,\rho) = \Delta\lambda_0^{\mathrm{r}}(T_0,\rho_0)F_\lambda(T,\rho) \tag{15}$$

$$F_\lambda(T,\rho) = f^{1/2}h^{-2/3}\left(\frac{M_0}{M}\right)^{1/2} \tag{16}$$

where $\Delta\lambda_0^{\mathrm{r}}$ are the residual thermal conductivity of the reference fluid R134a. They are calculated from the correlations developed by Perkins et al.[18].

2.2 Modification of the ECS model

The procedure presented above is completely predictive, and no experimental data thermal conductivity is used. McLinden et al. [12] showed that if an ECS model has additional parameters to slightly adjust the conformal density of a reference fluid, the prediction capabilities of the ECS model is signigicantly improved. In this work, such parameter is called a "thermal conductivity shape factor" for the thermal conductivity. The thermal conductivity shape factors β_λ, modify conformal densities of a reference fluid as follows:

$$\rho_{0,\mathrm{imp}} = \beta_\lambda \rho_0 \tag{17}$$

Generally, β_λ is given by the simple polynomial

$$\beta_\lambda = \sum_{b=0}^{n} d_b \left(\frac{\rho}{\rho_c}\right)^b \tag{18}$$

Experimental thermal conductivity data are used in this work to determine β_λ. Table 3 shows final values of the cofficients for R1336mzz(Z).

Table 3. Thermal conductivity shape factor

Coefficients	Thermal Conductivity Shape
d_0	0.88003
d_1	0.04187

3. RESULTS AND DISCUSSION

Thermal conductivities of R-1336mzz(Z) are calculated by density dependent exact shape factor and density independent empirical shape factor of ECS model individually and calculated values are compared with the experimental thermal conductivities measurement of Alam et al. [7]. For liquid, Alam et al.[7] measured thermal conductivities from temperature 314 K to 435 K and for pressure range from 0.5 MPa to 4 MPa. The corresponding values for vapor are from 321 K to 496 K & 0.1 MPa to 2 MPa. Calculated thermal conductivities of liquid at 2 MPa are compared with measured data to show the effect of various ECS models and shown in Fig. 2. Without thermal conductivity shape factor, calculated value is slight lower than the experimental value. However, ECS models predict the measured value significantly with the inclusion of the thermal conductivity shape. Calculated thermal conductivities of vapour at 0.1 Mpa are also compared with experimental thermal conductivities and shown in Fig. 3. Prediction of the two ECS models are similar as the contribution of residual component of thermal

conductivity is very low compare to the others contribution in vapour phase.

Fig. 4 shows the percentage deviation in thermal conductivity data between measured and predicted values by ECS method at liquid phase over the range of temperature 314 K to 435 K. The percent deviation of experimental fitted data with ECS model is better than ±2% with both exact and empirical shape factors. The deviations between the exact and empirical shape factors are small at lower temperature but significant change noticed at higher temperature. Therefore, it can be concluded that ECS model with exact shape factor is better than that with empirical especially at high temperature. The percentage deviation of experimental data of thermal conductivity at vapour phase against ECS model with exact shape factor has shown in Fig. 5. The temperature range for vapor phase is 321 K to 495 K. ECS model can predict most of the measured value within ±2%.

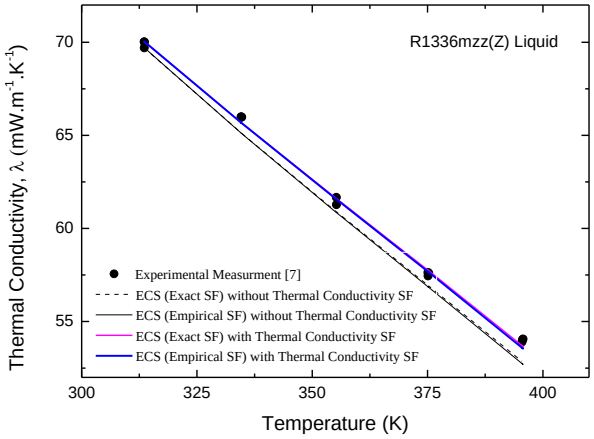

Fig. 2. Comparison of calculated and experimental thermal conductivities of liquid phase at 2 MPa.

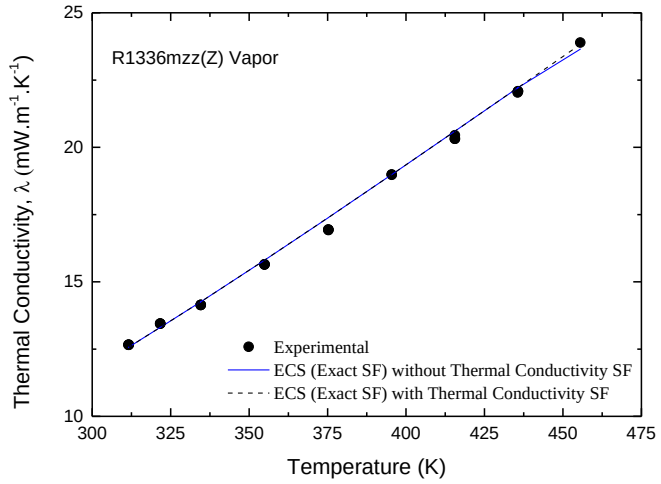

Fig. 3. Comparison of calculated and experimental thermal conductivities of vapor phase at 0.1 MPa.

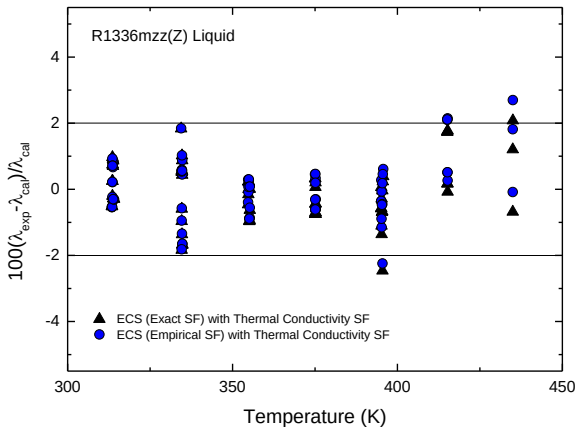

Fig. 4: Percentage deviations in the experimental liquid thermal conductivity data by Alam et al. [7] from calculated values with the ECS models.

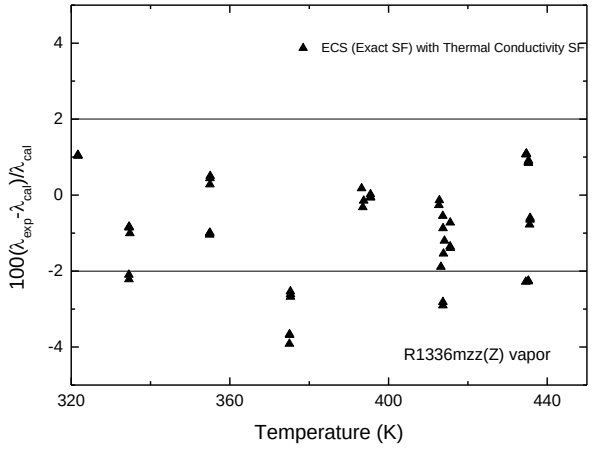

Fig. 5: Percentage deviations in the experimental vapour thermal conductivity data by Alam et al. [7] from calculated values with the ECS models.

4. CONCLUSION

ECS models were applied to model the thermal conductivity of R-1336mzz(Z). R134a is used as a reference fluid. Empirical shape factors were correlated from the vapor pressures and satured liquid densities of R-1336mzz(Z) and R134a. Exact shape factors were determined by solving equations for the comformal condition of both fluids. Comparisons with the experimental data showed that prediction capabilities of both ECS models are similar, and that if the thermal conductivity shape factors is introduced, the capabilities are significantly improved. In this case, typical deviations in the experimental data were ±2%.

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