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Transport properties of HFC and HFO based refrigerants using an excess entropy scaling approach

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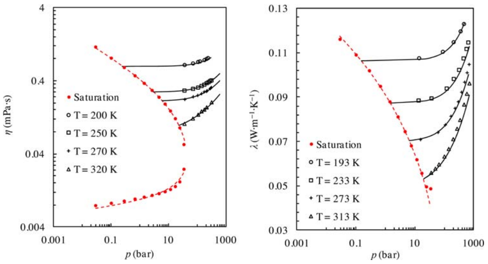
GRAPHICAL ABSTRACT



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ABSTRACT

The viscosity, thermal conductivity and Prandtl's number of HFC and HFO refrigerants were studied using an excess entropy scaling approach. Based on it, the complex temperature and pressure dependence of refrigerants under consideration were reduced to simple functions of the residual entropy computed using Polar PC-SAFT. The model coefficients were fitted to experimental data at saturated conditions and used to predict transport properties across a wide range of temperatures, up to 1000 bar. The model was able to capture the minimum in Prandtl's number observed near the critical point. The uncertainties in thermal conductivity predictions are comparable with those obtained with the well-correlated NIST REFPROP extended corresponding states approach (ECS), with maximum average deviations of around 3%. Moreover, predictions of the HFO refrigerants viscosities showed lower deviations than ECS. This work is a step forward in the development of predictive models for the design of optimal low GWP refrigerants.

1. Introduction

A global decision to phase out ozone depleting substances (ODS) such as hydrochlorofluorocarbons (HCFCs) and chlorofluorocarbons (CFCs) based on the Montreal Protocol was successfully made in 1987. Hydrofluorocarbons (HFCs), highly potent greenhouse gases (GHGs), were since then used as an alternative in refrigeration and air-conditioning equipment. However, according to the F-gas regulation, all vehicles sold in the European Union (EU) starting by 2017 must use a refrigerant that does not exceed a 100 year direct global warming potential (GWP) of 150 [1]. In comparison, 1,1,1,2-tetrafluoroethane (HFC-134a) which is most commonly used refrigerant in mobile air-conditioners has a GWP of 1300 [2]. Other HFCs share a GWP value of similar magnitude. The Kigali Amendment to the Montreal Protocol, a global deal signed in 2016 entering into force on 2019, legally binds world's nations to gradually phase out the consumption and production of HFCs by the late 2040s. The latter will significantly contribute to the Paris Agreement by avoiding nearly half a degree Celsius of temperature increase by the end of this century [3].

Extensive studies [4,5] were recently published by the National

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Institute of Standards and Technology (NIST) to screen thousands of candidate molecules to replace HFCs. Based on various environmental and thermodynamic criteria, hydrofluoroolefins (HFOs) were found to be the best available option so far. Moreover, a joint venture between Honeywell and Dupont was announced in 2007 to produce 2,3,3,3-tetrafluoropropene (HFO-1234yf) as a fourth generation alternative for HFC-134a in vehicles [6]. With a very low GWP of 4 [2], HFO-1234yf perfectly meets the current F-gas regulation target values. Other alternatives by Honeywell include the *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) with a GWP of 6 [2]. According to a roadmap report [7] published in 2014 by the United States (US) Department of Energy, highest priority in research should be given to explore and model the thermodynamic and heat transfer properties of new low GWP refrigerants.

Heat transfer and pressure drop characteristics in refrigeration systems are highly influenced by the working fluid transport properties. Accurate knowledge of the fluid viscosity, thermal conductivity and Prandtl's number is essential for determining its flow behavior, convection characteristics and two phase heat transfer and pressure drop in heat exchangers [8]. The highest accuracy representation for refrigerants transport properties are obtained through fluid specific correlations [9,10]. Aside from these fluid specific correlations, transport properties of refrigerants have been mainly modeled in the literature using extended corresponding states (ECS) [11–14], a method developed at NIST and implemented in its Reference Fluid Thermodynamic and Transport Property Database (REFPROP) [15]. The method implies mapping the transport properties for the fluid of interest onto a fluid with an accurate equation of state and transport property correlations. The method relies on obtaining a conformal state at which the reference fluid and the fluid of interest have the same residual Helmholtz free energy and compressibility factor. Bell and Laesecke [16] in NIST have recently taken a computationally faster approach by applying a modified version of Rosenfeld's entropy scaling theory [17] in combination with a corresponding states equation of state for 1-chloro-1,2,2,2-tetrafluoroethane (CFC-124) as a reference fluid to predict the viscosity of HFCs and HFOs. A theoretically, more rigorous, semi-empirical scheme was developed by Assael and Dymond [18] based on considerations of the hard sphere theory to predict the transport properties of liquids. The latter was employed by Gao et al. [19] to predict the viscosity and thermal conductivity of HFC containing mixtures with satisfactory accuracy. In terms of molecular theory, Llovell et al. [20] applied the free volume theory (FVT) coupled with the soft version of the statistical associating fluid theory (soft-SAFT) [21,22] to predict the viscosity of HFC refrigerants. Polishuk [23] coupled the SAFT + Cubic equation of state theory [24,25] with a modified version of the Yarranton-Satyro correlation [26] to estimate the viscosity of HFC-134a under extreme pressure conditions.

We present here a SAFT-based excess entropy scaling approach [33,34] to predict transport properties of several refrigerants, including: 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), HFC-134a, pentafluoroethane (HFC-125), hexafluoroethane (HFC-116), HFO-1234ze(E) and HFO-1234yf. This work belongs to a long term project on using molecular modeling tools for the rational design of new low GWP refrigerants. A molecular model based on the polar and perturbed chain form of the SAFT equation of state (Polar PC-SAFT) [27,28] in combination with the density gradient theory (DGT) [29,30] was presented in our previous publications [31,32] to predict the thermophysical (density, vapor pressure, isobaric heat capacity and speed of sound) and interfacial properties of HFC and HFO based refrigerants.

2. Molecular theory

2.1. Polar PC-SAFT equation of state

The Polar PC-SAFT equation of state [27,28] used in this work, as written for pure components in terms of the reduced Helmholtz free energy, is given as the sum of an ideal gas contribution, a^{id}, a hard-chain contribution, a^{hc}, a dispersion contribution, a^{disp}, and a dipolar contribution, a^{polar}:

$$a = a^{id} + a^{hc} + a^{disp} + a^{polar} \tag{1}$$

For the hard chain contribution, a^{hc}, Chapman et al. [35–37] developed an equation of state applicable for mixtures of hard-sphere chains comprising m segments.

$$a^{hc} = m_i a^{hs} - (m_i - 1)\ln g_i^{hs}(d_i) \tag{2}$$

where m_i is the number of segments (or spheres forming the chain) in a molecule of component i, $g_i^{hs}(d_i)$ is the radial pair distribution function at contact for segments of component i, d_i is the hard sphere diameter of component i, and the superscripts hc and hs indicate quantities of the hard-chain and hard-sphere systems, respectively.

The perturbation theory of Barker and Henderson [38] is used to calculate the contribution to the free energy due to van der Waals (dispersion) interactions between molecules, a^{disp}, using a set of equations for square-well potential function derived by Gross and Sadowski [39].

$$a^{disp} = -2\pi\rho\,[I_1(\eta, m_i)]\,m_i^2\left(\frac{\varepsilon_i}{k_B T}\right)\sigma_i^3 - \pi\rho m_i C_1\,[I_2(\eta, m_i)]\,m_i^2\left(\frac{\varepsilon_i}{k_B T}\right)^2\sigma_i^3 \tag{3}$$

and

$$C_1 = \left(1 + Z^{hc} + \rho\frac{\partial Z^{hc}}{\partial\rho}\right)^{-1} \tag{4}$$

where σ_i and ε_i donate the segment diameter and dispersion energy of component i respectively. The value of C_1 represents the compressibility of the hard chain fluid (Z^{hc}) and $I_1(\eta, m_i)$ and $I_2(\eta, m_i)$ are given by power series in density where the coefficients are functions of the chain length and the packing fraction, η

$$I_1(\eta, m_i) = \sum_{j=0}^{6} a_j(m_i)\eta^j \tag{5}$$

$$I_2(\eta, m_i) = \sum_{j=0}^{6} b_j(m_i)\eta^j \tag{6}$$

where the coefficients a_j and b_j depend on the chain length according to

$$a_j(m_i) = a_{0j} + \frac{m_i - 1}{m_i}a_{1j} + \frac{m_i - 1}{m_i}\frac{m_i - 2}{m_i}a_{2j} \tag{7}$$

$$b_j(m_i) = b_{0j} + \frac{m_i - 1}{m_i}b_{1j} + \frac{m_i - 1}{m_i}\frac{m_i - 2}{m_i}b_{2j} \tag{8}$$

The universal model constants for the a_{0j}, a_{1j}, a_{2j}, b_{0j}, b_{1j} and b_{2j} are tabulated in Gross and Sadowski's [39] work.

Finally, the change in free energy due to dipolar interactions, a^{polar}, is calculated using the Jog and Chapman theory [40,41] based on the dipolar term of Fischer and coworkers [42–44]. This term was obtained by dissolving all the bonds in a chain and then applying the u-expansion to the resulting mixture of polar and nonpolar spherical segments.

$$a^{polar} = \frac{a_2}{1 - a_3/a_2} \tag{9}$$

where a_2 and a_3 are the second- and third-order terms in the perturbation expansion. These terms have the following form

$$a_2 = -\frac{2\pi}{9}\frac{\rho}{(k_B T)^2}(m_i x_{p_i})^2\frac{\mu_i^4}{d_i^2}I_2 \tag{10}$$

$$a_3 = \frac{5}{162}\pi^2\frac{\rho^2}{(k_B T)^3}(m_i x_{p_i})^3\frac{\mu_i^6}{d_i^3}I_3 \tag{11}$$