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Helmholtz energy and extended corresponding states model for the prediction of thermodynamic properties of refrigerants

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ABSTRACT

This work was concerned with developing an accurate model for the prediction of thermodynamic properties of refrigerants. The work capitalised on previous works by the author about the development of accurate Helmholtz energy models for non-polar fluids, mixtures of those fluids and natural gas systems.

The proposed model was formulated in terms of the residual Helmholtz energy, which was expressed as the contribution of two terms: one from an extended corresponding states model and the other was a correction term. The extended corresponding states model was based on the temperature- and density-dependent correlations for shape factors that the author has presented previously in the literature, and the R-32 was chosen as the reference fluid. The correction term was a weighted term from the reference equation of state.

The fluids of interest were 19 refrigerants: R-11, R-12, R-22, R-41, R-113, R-116, R-123, R-124, R-125, R-134a, R-141b, R-142b, R-143a, R-152a, R-218, R-227ea, R-236ea, R-236fa and R-245fa. The following percentage overall absolute average deviations were obtained: 0.187 for $p\rho T$ data, 0.229 for saturation pressures, 0.206 for saturated-liquid densities, 1.053 for saturated-vapour densities, 1.734 for isochoric heat capacities, 1.238 for isobaric heat capacities and 0.662 for speeds of sound. These results showed an overall good agreement with the accuracy demanded of the equations for technical applications of refrigerants.

1. Introduction

The prediction of the thermodynamic properties of refrigerants and refrigerant mixtures is an active area of research because of the technological importance of those fluids and also because refrigerants are, in general, polar fluids, which is known to pose a demanding challenge on the predictive capabilities of thermodynamic models. Many equations of state (EoS) and models have been applied to that purpose, for instance, McLinden et al. [1] presented an overview of cubic equations, equations based on perturbation theory, the Benedict-Webb-Rubin equation, Helmholtz energy equations and extended corresponding states (ECS) models. Given the scope of this work, this section presents only a brief review of the application of Helmholtz energy and corresponding states models.

In the decade of the 1990s, multiparameter equations of state were developed for 11 refrigerants. Those models are the fundamental (Helmholtz energy) equations by Marx et al. [2] for R-11 (trichlorofluoromethane), R-12 (dichlorodifluoromethane) and R-113 (1,1,2-trichlorotrifluoroethane), Wagner et al. [3] for R-22 (chlorodifluoromethane), Tillner-Roth and Yokozeki [4] for R-32 (difluoromethane), de Vries et al. [5] for R-124 (1-chloro-1,2,2,2-tetrafluoroethane), Tillner-Roth and Baehr [6] for R-134a (1,1,1,2-tetrafluoroethane) and Lemmon and Jacobsen [7] for R-143a (1,1,1-trifluoroethane) and the equations explicit in pressure by Younglove and McLinden [8] for R-123 (2,2-dichloro-1,1,1-trifluoroethane), Piao and Noguchi [9] for R-125 (pentafluoroethane) and Outcalt and McLinden [10] for R-152a (1,1-difluoroethane). As reference EoSs, those models comprise functional forms of around 20 adjustable coefficients, were optimised over large sets of high-quality data for a number of thermodynamic properties and are accurate to within the experimental uncertainty. More recently, Span and Wagner [11] applied to the above fluids, excluding R-124, the so-called "technical equations of state", that are Helmholtz energy models but with only 12 adjustable coefficients. The technical equations are easier to develop for fluids with limited amounts of high-quality data and are meant to meet the accuracy required for

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technical application, i.e. process design, simulation and control and equipment design. Later on, Lemmon and Span [12] extended those models to six additional refrigerants: R-116 (hexafluoroethane), R-141b (1,1-dichloro-1-fluoroethane), R-142b (1-chloro-1,1-difluoroethane), R-218 (octafluoropropane), R-245fa (1,1,1,3,3-pentafluoropropane) and R-41 (fluoromethane). For these models, the limits on percentage accuracy are: for densities: within 0.2 for $p \leq 30$ MPa and within 0.5 for $p > 30$ MPa; for speeds of sound and isobaric heat capacities: within 1 for gaseous and gas-like supercritical states at $p \leq 30$ MPa and within 2 for liquid and liquid-like states at $p \leq 30$ MPa, and within 2 for all states at $p > 30$ MPa; within 0.2 for saturation pressures and saturated-liquid densities and within 0.4 for saturated-vapour densities.

Regarding refrigerants, the application of corresponding states and ECS models has been very limited. Huber and Ely [13] presented an ECS model with shape factors depending only on temperature. More recently, Scalabrin et al. presented a three-parameter corresponding states model [14] with R-12 and R-32 as the reference fluids and a modified scaling parameter, and an ECS model coupled with a neural network [15].

Recently, the author presented [16] a model for non-polar fluids whereby the residual Helmholtz energy was expressed as the contribution of two terms, one from an ECS model and the other was a temperature- and density-dependent correction term. For a set of 19 fluids, that model proved to have the same predictive capabilities of the technical equations. On further extension to mixtures of those fluids [17,18], the Helmholtz energy model by Estela-Uribe also showed to be as accurate as the reference Helmholtz energy mixture model by Lemmon and Jacobsen [19] and the reference EoS by Kunz et al. [20] for natural gas systems.

From the above, the purpose of this work was to apply to refrigerants, and further to refrigerant mixtures, the methodology of the model of [16] and meet the required accuracy of the technical equations indicated above. The rationale for this approach was that as the ECS model gives a close approximation to the fluid residual Helmholtz energy, then the combination with an appropriate correction term should enable the model to meet the abovementioned accuracy. The basic hypothesis was that an ECS model of the same structure, i.e. with the same shape factors model, as that used in [16], could be used to this purpose provided the choice of an appropriate reference fluid. All in all, the overall intent of this work was to prove the predictive capabilities of ECS models with regards to polar fluids, at least the particular application to refrigerants.

The proposed model used the reference EoS by Tillner-Roth and Yokozeki [4] for R-32 as the reference model fluid, the reasons for this choice are presented in section 3. The model was applied to 19 refrigerants: 4 from the methane series (R-11, R-12, R-22, and R-41), 10 from the ethane series (R-113, R-116, R-123, R-124, R-125, R-134a, R-141b, R-142b, R-143a and R-152a) and 5 from the propane series (R-218, R-227ea, R-236ea, R-236fa and R-245fa). The chlorofluorocarbons R-11, R-12 and R-113, whose industrial production was banned because of their ozone depletion potential, were included as that was necessary to construct a model valid for a wide range of fluids (see the details in Sections 3 and 4). Deviations between calculated properties and experimental data were calculated for $p\rho T$ data, saturation pressures, orthobaric densities, isochoric and isobaric heat capacities and speeds of sound. The overall percentage average absolute deviations (AAD) were: 0.187 for $p\rho T$ data, 0.229 for saturation pressures, 0.206 for saturated-liquid densities, 1.053 for saturated-vapour densities, 1.734 for isochoric heat capacities, 1.238 for isobaric heat capacities and 0.662 for speeds of sound. Thus, the results showed an overall good agreement with the accuracy demanded of the technical equations for refrigerants.

2. Theory

The ECS theory is well known since the works by Cook and Rowlinson [21] and Leach et al. [22] and herein a summary is reproduced from previous publications by the author, for instance [23]. The corresponding states condition between a fluid of interest and a reference fluid is expressed by equating two configurational properties between those fluids:

$$Z(T, \rho) = Z_0(T/f, h\rho), \tag{1}$$

$$\Phi^{\text{res}}(T, \rho) = \Phi_0^{\text{res}}(T/f, h\rho) \tag{2}$$

In Eqs. (1) and (2), Z is the compression factor, $\Phi^{\text{res}} = A^{\text{res}}/nRT$ is the dimensionless residual Helmholtz energy, the subscript '0' denotes the reference fluid and f and h are the so-called "equivalent substance reducing ratios" that map the properties of the fluid of interest onto those of the reference fluid at the scaled conditions $T_0 = T/f$ and $\rho_0 = h\rho$. The simple corresponding states principle (CSP) asserts that the configurational properties of two fluids must be equal at the same reduced conditions, thus, f and h would be the simple ratios $f = T^c/T_0^c$ and $h = \rho_0^c/\rho^c$. However, the CSP is valid only for conformal fluids, i.e. fluids with intermolecular potentials of the same functional form. To account for departures from conformality due to molecular geometry, temperature- and density-dependent shape factors θ and φ are introduced to correct the equivalent substance reducing ratios. This procedure is the macroscopic analogy of the introduction of temperature- and density-dependent effective spherical intermolecular potential parameters. Thus:

$$f = (T^c/T_0^c)\theta(T_r, \rho_r), \tag{3}$$

$$h = (\rho_0^c/\rho^c)\varphi(T_r, \rho_r). \tag{4}$$

Here, the subscript 'r' indicates reduced properties. The shape factors could be calculated by solving simultaneously the equations of state of the two fluids at any state point. However, as the practical value of ECS models is to calculate properties of fluids for which an EoS is not known, the shape factors are obtained from temperature- and density-dependent correlations.

3. Proposed model

Following the work of [16], the residual Helmholtz energy was expressed as:

$$\Phi^{\text{res}}(\tau, \delta) = \Phi_{\text{ECS}}^{\text{res}}(\tau, \delta) + \Delta\Phi^{\text{res}}(\tau, \delta) \tag{5}$$

where $\Phi_{\text{ECS}}^{\text{res}}$ is the contribution from an ECS model, $\Delta\Phi^{\text{res}}$ is a correction term, $\delta = \rho/\rho^c$ is the reduced density and $\tau = T^c/T$ is the inverse reduced temperature. In this work, the residual Helmholtz energy was formulated as:

$$\Phi^{\text{res}}(\tau, \delta) = \Phi_0^{\text{res}}(\tau_0, \delta_0) + d(\omega' - \omega_0)\Phi_0^{\text{res}}(\tau, \delta) \tag{6}$$

In Eq. (6) the first term on the right-hand side is the ECS contribution, i.e. the residual Helmholtz energy of the reference fluid evaluated at the scaled reduced conditions τ_0 and δ_0, d is an adjustable parameter, ω is an adjustable parameter in lieu of the acentric factor ω' and ω_0 is the acentric factor of the reference fluid. Following the definitions of the equivalent substance reducing ratios and Eqs. (3) and (4), the scaled reduced conditions of the reference fluid are given by the simple relationships $\tau_0 = \theta\tau$ and $\delta_0 = \varphi\delta$.

The second term in the right-hand side of Eq. (6) is the correction to the residual Helmholtz energy. The rationale to formulate such a correction as in Eq. (6) was the need to provide a more capable correction than that used in the work of [16], which was a simple product of δ^2 and τ. Preliminary trials proved that a model with that