International Journal of Thermophysics, Vol. 26, No. 2, March 2005 (© 2005)
DOI: 10.1007/s10765-005-4507-8

Modeling Alkane and Haloalkane Mixture Viscosities in a Three-Parameter Corresponding States Format[1]

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The fundamental structure of the model is based upon a detailed and innovative conformality analysis of the viscosity surfaces of pure fluids similar to that proposed for thermodynamic properties [G. Scalabrin et al. *Fluid Phase Equilib.* **170**:23 (2000); *Int. J. Refrig.* **26**:35 (2003)], resulting in the introduction of a new specific scaling parameter ψ for viscosity, defined by a single experimental viscosity value. The model structure is based on two reference fluids for which pure-fluid viscosity dedicated equations (VDE) are available, which in this work are *ethane* and *propane*. The model is then extended to mixtures following the classical corresponding states (CS) *one fluid model* using mixing rules without interaction parameters. This gives the model a predictive character. It can be reliably applied in a wide range of pressure–temperature values, in both liquid and vapor phases, due to the validity ranges of the reference equations. The investigated mixtures include binary and multicomponent systems of both light and heavy *n*-alkanes and halogenated alkanes including R134a, R125, R152a, R143a, R22, R142b, R32, and R124 as components. For both families of fluids, the accuracy in terms of absolute average deviation (AAD) is within 2.68% in the vapor phase and 3.0% in the liquid phase. The model has also been validated for strongly azeotropic mixtures such as R32–R290 and R134a–R290 giving interesting results by fitting the interaction parameters on a limited subset of data. The effectiveness of the proposed procedure is enhanced by the comparison with a recently published advanced theoretical model.

KEY WORDS: alkanes; corresponding states; dedicated equations; halogenated alkanes; multicomponent mixtures; predictive model; three parameters; transport properties; viscosity.

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[1] Paper presented at the Sixteenth European Conference on Thermophysical Properties, September 1–4, 2002, London, United Kingdom.

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0195-928X/05/0300-0429/0 © 2005 Springer Science+Business Media, Inc.

1. INTRODUCTION

The availability of predictive methods to calculate thermophysical properties of fluid mixtures has aroused great interest in those branches of engineering requiring reliable properties for optimal design purposes. The field of refrigerant applications has greatly increased the need for the characterization of substitute mixtures for the banned pure fluids. The lack of experimental data for a wide range of mixtures has hindered the development of high accuracy correlative models; whereas the application conditions and the large number of possible mixtures make it impossible to proceed by experimental means only.

In this light, the development of predictive models becomes very important. At present the corresponding states (CS) approach is suitable for predictive models. In particular, it has been widely applied in the extended corresponding states (ECS) format to calculate the viscosity of hydrocarbon mixtures [2] and the viscosity of refrigerants [2]. However, as the accuracy of these models greatly depends on the availability of the experimental data used to improve fluid specific correlations, these models become quite similar to estimation methods.

The aim of this work is to investigate the possibility of extending to mixtures a predictive model successfully proposed for thermodynamic properties [4, 18, 49] and viscosity of pure fluids [5, 17]. Requiring only the critical constants and a single saturated liquid viscosity value for each mixture component, the model presents a predictive character. Furthermore, the effectiveness of the CS principle when applied to mixtures of homologous fluids, such as the alkanes and haloalkanes of the present study, is demonstrated.

The results for a consistent number of binary and multicomponent mixtures, both in liquid and in vapor phases, are discussed pointing out the high accuracy of the model and its predictive character. The proposed work can be regarded as a suitable tool to calculate the viscosity of mixtures as well as an interesting procedure to follow in those technical applications where thermophysical properties need to be determined through a predictive approach.

2. EXISTING MODELS

Currently, the most promising models present a theoretical framework based on rigid sphere theory proposed by Vesovic and Wakeham [3, 6] and Vesovic et al. [7]. The original scheme was developed to predict the viscosity of nonpolar mixtures, for which the model reaches a high accuracy, particularly at supercritical conditions. This model successfully predicts the vapor phase viscosity for polar mixtures as well, but for liquid states the accuracy decreases because the rigid-sphere approach does not take polarity effects into account.

Preliminary results of the model applied to the liquid phase have been recently presented by Vesovic [8], limiting the calculation along the liquid saturation line. The validation has been specifically referred to strongly polar and non-ideal refrigerant mixtures. For mixtures containing molecules of similar size the results are remarkably good, while for highly nonideal and azeotropic mixtures the accuracy rapidly decreases.

To predict the viscosity of mixtures in the liquid phase at high pressures, an approach based on hard-sphere theory has been proposed by Assael et al. [9] restricting the application of a previous pure component model to mixtures of homologous series. This approach has the advantage of using the parameters of the pure components, making the model purely predictive. In recent papers Assael et al. [10, 11] used the hard-sphere theory to modify the previous Vesovic and Wakeham theoretical scheme and extended it to liquid mixture prediction. A significant test of this approach has been recently presented by Assael et al. [12] reporting the prediction results of a wide range of mixtures with different components including hydrocarbons, alcohols, and halogenated refrigerants. The consistent accuracy obtained on a number of those mixtures demonstrates the sound basis of such a theoretical approach. However, this model requires specific inputs: the viscosity and the molar density of the pure components and the mixture molar density at the same conditions of the mixture. This makes the model difficult to apply extensively.

Several viscosity models can be regarded as *semi-theoretical* due to the use of a specific parameter regressed on experimental data and setup on a theoretical framework. These models assume the generalized CS principle approach originally applied to thermodynamic properties by Lee and Kesler [13] and then proposed by Teja and Rice [14] to calculate the viscosity of pure fluids in the liquid phase. These models, regressed on experimental data, can be simply regarded as correlations $\eta = \eta\ (T)$ only effective for liquid-phase conditions, where the pressure effect is negligible. These models cannot therefore be applied to vapor states or to states in the supercritical region.

According to an improved approach of the CS model, Ely and Hanley [1] introduced the ECS method giving satisfactory results for *n*-alkanes. For isomeric paraffins and polar fluids its accuracy is rather poor, both for pure components and for mixtures. The original ECS model was then modified by Ely [15] introducing fluid specific parameters, the *shape* and *scaling* factors, which yield better results particularly when applied to polar fluids such as haloalkanes. A further modification by Klein et al. [16] of the ECS model framework introduces a third fluid specific shape factor regressed on pure fluid viscosity. This last ECS model for mixtures requires the viscosity equation and the equation of state of the reference fluid; together with the equation of state, the critical properties, and the acentric factor of each of the mixture components. Due to these requirements, this model follows a correlative approach requiring the input of many properties, among which some are difficult to access in the case of a scarcely studied component.

A large number of viscosity models could be further cited here. For clarity it is important to emphasize that the majority are not strictly predictive as they require mixture data to determine component parameters or interaction parameters.

3. PROPOSED MODEL

The mixture model proposed here is based on a format that is similar to the formalism developed by the authors for pure fluids. As this work specifically focuses on mixtures, only a brief description of the pure fluid model is presented here making reference to a recent work [5] for a detailed review of the fundamentals. The basic idea of that model comes from a conformality analysis of the pure component viscosity surfaces which allows the extension of the three-parameter CS approach to transport properties. Up to recent times, the CS approach has been mostly applied only to thermodynamic properties. The high conformality level of the reduced viscosity surfaces suggests a new *third parameter* specific for viscosity. The new individual *scaling factor* ψ_i for viscosity is defined as:

$$\psi_i = \left(\log \eta_\mathrm{r}^\mathrm{lsat} |_i - \log \eta_\mathrm{r}^\mathrm{lsat} \Big|_\mathrm{ref} \right)_{T_\mathrm{r}} \tag{1}$$

where $\eta_\mathrm{r}^\mathrm{lsat}|_i$ is the reduced viscosity value of a fluid of interest referred to saturated liquid conditions at a fixed reduced temperature T_r, whereas $\eta_\mathrm{r}^\mathrm{lsat}\big|_\mathrm{ref}$ is the corresponding value for a selected reference fluid, evaluated at the same T_r. To get the individual ψ_i values, Eq. (1), experimental saturated liquid viscosity data at the selected value of T_r are needed for both the reference fluid and the fluid of interest. For the mixture components involved in this work and with *methane* as the reference fluid, the ψ_i values are given in Table I.

Viscosity is reduced through a pseudo-critical viscosity value H_c:

$$\eta_r = \frac{\eta}{H_\mathrm{c}} \quad \text{with} \quad H_\mathrm{c} = \frac{M^{1/2} P_c^{2/3}}{R^{1/6} A^{1/3} T_\mathrm{c}^{1/6}} \tag{2}$$

where M is the molar mass, P_c and T_c are the critical pressure and temperature, A is Avogadro's number, and R is the universal gas constant.

Table I. Values of Viscosity Individual Scaling Factor ψ_i for the Components of the Mixtures Studied here, with Methane as Reference Fluid

Fluid	ψ_i	Fluid	ψ_i
Methane[a]	0.0000	R141b	0.2224
Ethane[a]	0.0759	R124	0.2754
Propane[a]	0.1329	R123*	0.2518
i-butane	0.1867	R125	0.2767
n-butane[a]	0.1527	R32	0.1566
n-pentane	0.1661	R22	0.1813
n-hexane	0.1934	R134a*	0.2681
n-heptane[a]	0.2098	R142b	0.2161
n-octane	0.2349	R152a*	0.2016
n-nonane	0.2665	R143a	0.2117
n-decane	0.2882		
n-undecane	0.3112		
n-dodecane	0.3270		
n-tridecane	0.3487		
n-pentadecane	0.3602		

[a] Pure-fluid viscosity equation available.

If in a range of T_r, the ψ_i scaling factor can be considered as independent from T_r, and knowing the $\log \eta_\mathrm{r}^\mathrm{lsat}(T_\mathrm{r})\big|_\mathrm{ref}$ function, any other $\eta_\mathrm{r}^\mathrm{lsat}(T_\mathrm{r})\big|_i$ function can be obtained from linear scaling through ψ_i. For conformal fluids at each T_r a plot of the saturated liquid viscosity vs. ψ_i tends to fall onto a straight line, as shown in Fig. 1. Thus, the saturated liquid viscosity of a target fluid can be obtained by interpolation, by means of ψ_i, of the viscosity of two reference fluids at the same T_r. Assuming that the linear scaling is maintained away from the saturated liquid condition, that is for the liquid, vapor, and supercritical regions; namely,

$$\psi_i\,(T_\mathrm{r}, P_\mathrm{r})\big|_{\substack{\mathrm{liq}\\ \mathrm{vap}\\ \mathrm{scrit}}} = \psi_i\big|_{T_\mathrm{r}}^{\mathrm{sl}} = \mathrm{const} \tag{3}$$

the former results can be extended to the whole $\eta_\mathrm{r} T_\mathrm{r} P_\mathrm{r}$ surface. Maintaining the general scheme applied for the three parameter CS model, this model is based on two reference fluids. They are selected on the basis of their viscosity equations, and use an interpolation criterion based on their $\psi^{\mathrm{r}1}$ and $\psi^{\mathrm{r}2}$ values.

Given the reduced viscosities of the reference fluids, $\eta_\mathrm{r}^{\mathrm{r}1}$ and $\eta_r^{\mathrm{r}2}$, the reduced viscosity of a fluid of interest, η_{ri}, can be represented by

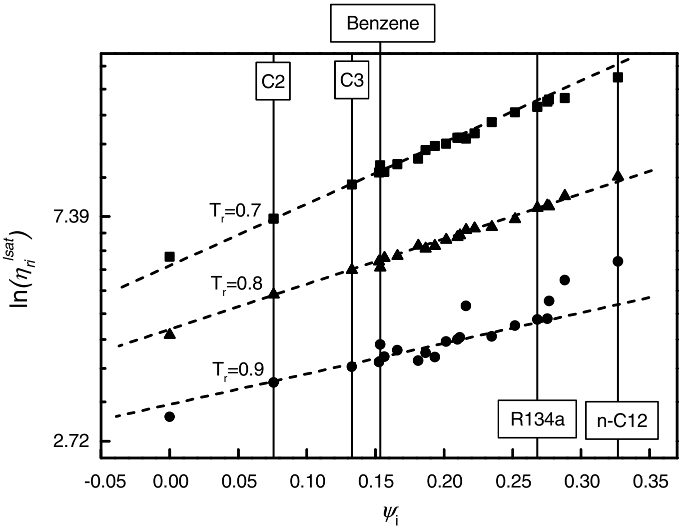


Fig. 1. Saturated liquid reduced viscosity $\eta_{\mathrm{ri}}^{\mathrm{lsat}}$ vs. ψ_i for some hydrocarbons and haloalkanes at different T_{r} values.

$$\eta_{\mathrm{ri}}\left(T_{\mathrm{r}}, P_{\mathrm{r}}, \psi_i\right)=\eta_{\mathrm{r}}^{\mathrm{r1}}+\frac{\psi_i-\psi^{\mathrm{r1}}}{\psi^{\mathrm{r2}}-\psi^{\mathrm{r1}}}\left(\eta_{\mathrm{r}}^{\mathrm{r2}}-\eta_{\mathrm{r}}^{\mathrm{r1}}\right) \tag{4}$$

where the superscripts r1 and r2 refer to the reference fluids. The viscosity equations are expressed as functions of temperature and density, $\eta=\eta(T, \rho)$, so that to solve Eq. (4) the following procedure is needed. At a given T and P, the reduced T_{r} and P_{r} of the target fluid are determined, and these values allow the equations of state of the reference fluids to be solved:

$$\begin{cases} P_{\mathrm{r}}=P_{\mathrm{r}}^{\mathrm{r1}}\left(T_{\mathrm{r}}, \rho_{\mathrm{r}}^{\mathrm{r1}}\right) \\ P_{\mathrm{r}}=P_{\mathrm{r}}^{\mathrm{r2}}\left(T_{\mathrm{r}}, \rho_{\mathrm{r}}^{\mathrm{r2}}\right) \end{cases} \tag{5}$$

to implicitly obtain the reduced density variables $\rho_{\mathrm{r}}^{\mathrm{r1}}$, $\rho_{\mathrm{r}}^{\mathrm{r2}}$. From these values, the reduced viscosities of the reference fluids can be determined through their corresponding viscosity equations:

$$\begin{cases} \eta_{\mathrm{r}}^{\mathrm{r1}}=\eta_{\mathrm{r}}^{\mathrm{r1}}\left(T_{\mathrm{r}}, \rho_{\mathrm{r}}^{\mathrm{r1}}\right) \\ \eta_{\mathrm{r}}^{\mathrm{r2}}=\eta_{\mathrm{r}}^{\mathrm{r2}}\left(T_{\mathrm{r}}, \rho_{\mathrm{r}}^{\mathrm{r2}}\right) \end{cases} \tag{6}$$

which can be used to solve Eq. (4) for the reduced viscosity of the fluid of interest, η_{ri}.

The format of the model for pure fluids, expressed by Eq. (4), can be used for mixtures by applying a *one-fluid-model* approach. This procedure modifies the critical properties of the pure fluids introducing pseudo-critical mixture parameters T_{cmix}, P_{cmix}, and ψ^{mix}, which are obtained from mixing rules having only the composition variable.

Considering the accurate results obtained in a previous work devoted to thermodynamic properties [4, 18, 49], this format is extended here to transport properties using the mixing rules by Wong et al. [19, 20], applied to the present CS model:

$$T_{\mathrm{cmix}} / P_{\mathrm{cmix}} = \sum_i \sum_j x_i x_j T_{cij} / P_{cij} \tag{7}$$

$$T^2_{\mathrm{c\,mix}} / P_{\mathrm{c\,mix}} = \sum_i \sum_j x_i x_j T^2_{cij} / P_{cij} \tag{8}$$

$$T_{cij} = \alpha_{ij} \left(T_{ci} T_{cj}\right)^{1/2} \tag{9}$$

$$P_{cij} = 8T_{cij} \Big/ \left\{ \beta_{ij} \left[\left(T_{ci} / P_{ci} \right)^{1/3} + \left(T_{cj} / P_{cj} \right)^{1/3} \right]^3 \right\} \tag{10}$$

$$\psi^{\mathrm{mix}} = \sum_i x_i \psi_i \tag{11}$$

where the subscript c refers to the critical value of each of the mixture components. Furthermore, it is $\alpha_{ij} = \alpha_{ji}$ and $\beta_{ij} = \beta_{ji}$.

Once these quantities are known, the mixture model has a structure quite similar to that of the previous Eq. (4) for pure fluids:

$$\eta_{\mathrm{r}}^{\mathrm{mix}} (T_{\mathrm{r}}, P_{\mathrm{r}}, \bar{x}) = \eta_{\mathrm{r}}^{\mathrm{r1}} + \frac{\psi^{\mathrm{mix}} - \psi^{\mathrm{r1}}}{\psi^{\mathrm{r2}} - \psi^{\mathrm{r1}}} \left(\eta_{\mathrm{r}}^{\mathrm{r2}} - \eta_{\mathrm{r}}^{\mathrm{r1}} \right) \tag{12}$$

with the same meanings for the superscripts r1 and r2 and with the superscript mix indicating the mixture property.

For each binary mixture, the mixing rules include two adjustable interaction coefficients, α_{ij} and β_{ij}, that can be regressed on sets of mixture viscosity data, making the model *correlative*. If these coefficients are set to unity, the model becomes *predictive* and experimental viscosity data for the mixture are not used in the development of the model. For most mixtures investigated in this work, the predictive version of the model provides sufficient accuracy.

4. CHOICE OF REFERENCE FLUIDS

As a matter of fact, the choice of the two reference fluids r_1 and r_2 is important for the performance of the model and it is not to be confused with the choice of the fluid assumed for defining the individual *scaling factor* ψ_i in Eq. (1), i.e., *methane* in the present case. Since differences between the scaling factors ψ_i, rather than absolute values, are involved in the model structure, it is possible to select any fluid for the definition of ψ_i. Considering that the structure of the model is based on the interpolation of the viscosity surfaces of two *reference* fluids, the choice of these fluids has to satisfy some fundamental requirements:

- Availability of an accurate dedicated viscosity equation $\eta_r = \eta_r(T_r, \rho_r)$ for each of the reference fluids;
- Availability of a high accuracy dedicated equation of state to convert the independent variables from T, P to T, ρ;
- Wide validity ranges of the viscosity equation and of the equation of state in the T_r, P_r domain.

Besides these requirements, the reference fluids need to be as representative as possible of the fluid properties in term of conformal behavior. Because through the reference fluid scaling parameters, ψ^{r1} and ψ^{r2}, the viscosity values of the two selected reference fluids are interpolated, the reference fluids must have the greatest degree of alignment with any other fluid of the family, in a viscosity versus ψ_i diagram. Such behavior can be easily verified given experimental viscosity data at saturation. The conformality can be obviously verified also at non-saturated condition, assessing the alignment of viscosity values for different fluids at same T_r, P_r. This is shown in Fig. 1 within the limits of the saturated liquid boundary, due to the difficulty to find, for each fluid, experimental data at the same T_r, P_r conditions. It is evident that the viscosity data tend to fall on a straight line and, as a consequence, different pairs of fluids can be selected as references. Nevertheless, the suitable number of component pairs to be used as references is limited, since a VDE and an EoS have to be available for them.

The importance of the alignment of the mixture viscosity data with the viscosity of reference fluids is highlighted in the following example. The model has been applied to a multicomponent mixture of alkanes selecting different reference fluid pairs. Comparing the results in Table II and examining the viscosity distribution illustrated in Fig. 2, it is evident that the more the reference fluids are aligned with the viscosity of the mixture, the more accurate is the model. The reference pairs with better alignment with the mixture reduced viscosity are indicated in Table II in bold font. The experimental data are from Abe et al. [21].

Considering the binary mixtures, we have decided to choose always one or both components as reference fluids, when they have viscosity

Table II. Results for the Alkane Mixture C1 + C2 + C3 + *n*-C4 with Different Reference Fluids; Data from Ref. [21][a]

Mixture	Reference 1	Reference 2	AAD (%)	Max (%)
C1 + C2 + C3 + *n*-C4	**C1**	**C2**	1.25	1.51
	C1	C3	1.51	2.07
	C1	*n*-C4	3.07	3.41
	C2	**C3**	1.38	1.52
	C2	C4	2.01	3.87
	C3	C4	3.24	4.85

[a] AAD = absolute average deviation, Max = maximum deviation.

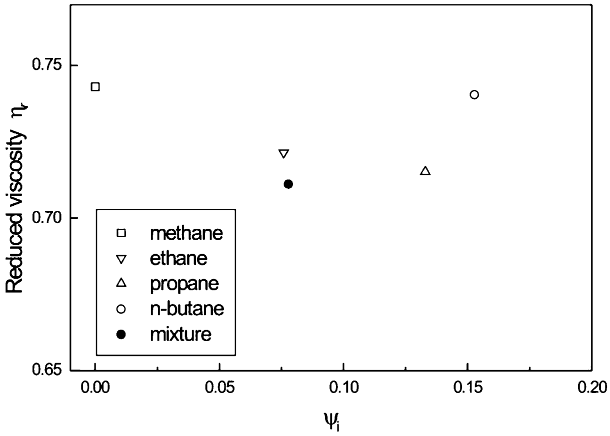
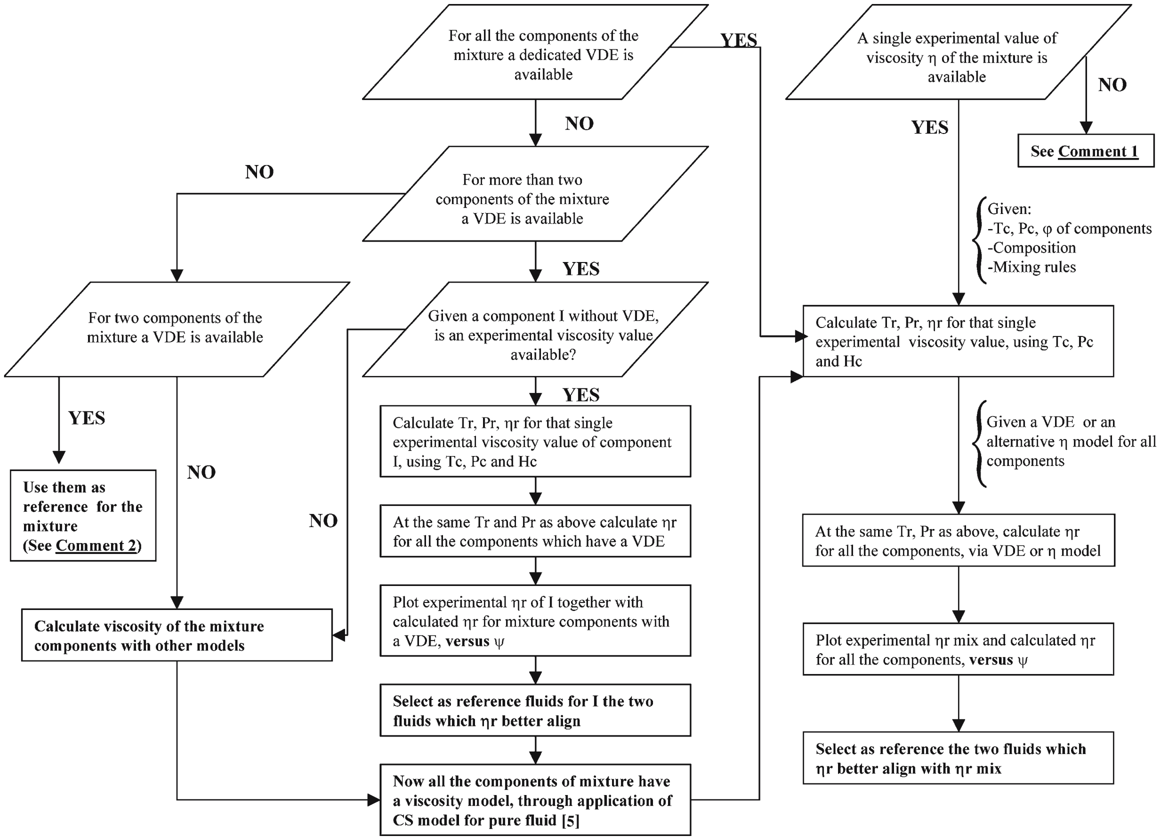


Fig. 2. Values of reduced viscosity η_r for the components C1, C2, C3, *n*-C4, and their mixture vs. the scaling parameter ψ_i and data from Ref. [21].

equations available. The components of the mixture, then, are expected to be aligned with the mixture viscosity. When this is not verified, as for strongly polar mixtures showing, for example, vapor–liquid equilibrium with azeotropic behavior, then interaction parameters have to be regressed, as it will be shown later.

In the case of multicomponent mixtures the suggested procedures for the selection of the appropriate pair of reference fluids are reported in the following flowchart.


For all the components of the mixture a dedicated VDE is available
YES
A single experimental value of viscosity η of the mixture is available
NO
See Comment 1
YES
NO
For more than two components of the mixture a VDE is available
NO
YES
Given:
-Tc, Pc, φ of components
-Composition
-Mixing rules
For two components of the mixture a VDE is available
Given a component I without VDE, is an experimental viscosity value available?
Calculate Tr, Pr, ηr for that single experimental viscosity value, using Tc, Pc and Hc
YES
YES
Calculate Tr, Pr, ηr for that single experimental viscosity value of component I, using Tc, Pc and Hc
Given a VDE or an alternative η model for all components
Use them as reference for the mixture (See Comment 2)
NO
NO
At the same Tr and Pr as above calculate ηr for all the components which have a VDE
At the same Tr, Pr as above, calculate ηr for all the components, via VDE or η model
Calculate viscosity of the mixture components with other models
Plot experimental ηr of I together with calculated ηr for mixture components with a VDE, versus ψ
Plot experimental ηr mix and calculated ηr for all the components, versus ψ
Select as reference fluids for I the two fluids which ηr better align
Select as reference the two fluids which ηr better align with ηr mix
Now all the components of mixture have a viscosity model, through application of CS model for pure fluid [5]

From the preceding, some remarks have to be added to facilitate the understanding of the proposed procedure. Two comments are, in particular, relevant.

Comment 1. At least one experimental viscosity value at temperature T and pressure P is necessary for the mixture. On the other hand, if no data are available, the discussion on the performance of a model with different reference fluids or even of different models is meaningless for lack of experimental evidence.

Comment 2. In the case only two components have a VDE, the choice is straightforward; those two fluids are the reference fluids. It can be argued that those two fluids can be used to build up the viscosity of all the components of the mixture. This leads to a redundant calculation:

- Let a and b be two mixture components, arbitrarily chosen as references in the mixture model; they are indicated with subscripts a and b.
- Let the subscripts 0 and 1 indicate the two reference fluids used in calculating the viscosity of components a and b with the mixture model.
- Let the superscript *mix* indicate the mixture and the subscript r the reduced values.

The proposed mixture model is

$$\eta_{\mathrm{r}}^{\mathrm{mix}} = \eta_{\mathrm{r}}^{\mathrm{a}} + \frac{\psi^{\mathrm{mix}} - \psi^{\mathrm{a}}}{\psi^{\mathrm{b}} - \psi^{\mathrm{a}}}\left(\eta_{\mathrm{r}}^{\mathrm{b}} - \eta_{\mathrm{r}}^{\mathrm{a}}\right) \tag{13}$$

but for the pure components a and b, it is

$$\eta_{\mathrm{r}}^{\mathrm{a}} = \eta_{\mathrm{r}}^{0} + \frac{\psi^{\mathrm{a}} - \psi^{0}}{\psi^{1} - \psi^{0}}\left(\eta_{\mathrm{r}}^{1} - \eta_{\mathrm{r}}^{0}\right) \tag{14}$$

$$\eta_{\mathrm{r}}^{\mathrm{b}} = \eta_{\mathrm{r}}^{0} + \frac{\psi^{\mathrm{b}} - \psi^{0}}{\psi^{1} - \psi^{0}}\left(\eta_{\mathrm{r}}^{1} - \eta_{\mathrm{r}}^{0}\right) \tag{15}$$

Combining Eqs. (13), (14), and (15), one get

$$\begin{aligned}\eta_{\mathrm{r}}^{\mathrm{mix}} = \eta_{\mathrm{r}}^{0} + \frac{\psi^{\mathrm{a}} - \psi^{0}}{\psi^{1} - \psi^{0}}\left(\eta_{\mathrm{r}}^{1} - \eta_{\mathrm{r}}^{0}\right) + \frac{\psi^{\mathrm{mix}} - \psi^{\mathrm{a}}}{\psi^{\mathrm{b}} - \psi^{\mathrm{a}}}\Bigg\{\eta_{\mathrm{r}}^{0} + \frac{\psi^{\mathrm{b}} - \psi^{0}}{\psi^{1} - \psi^{0}}\left(\eta_{\mathrm{r}}^{1} - \eta_{\mathrm{r}}^{0}\right) \\ - \left[\eta_{\mathrm{r}}^{0} + \frac{\psi^{\mathrm{a}} - \psi^{0}}{\psi^{1} - \psi^{0}}\left(\eta_{\mathrm{r}}^{1} - \eta_{\mathrm{r}}^{0}\right)\right]\Bigg\}\end{aligned} \tag{16}$$

which results in

$$\eta_{\mathrm{r}}^{\mathrm{mix}} = \eta_{\mathrm{r}}^{0} + \frac{\psi^{\mathrm{mix}} - \psi^{0}}{\psi^{1} - \psi^{0}} \left(\eta_{\mathrm{r}}^{1} - \eta_{\mathrm{r}}^{0}\right) \tag{17}$$

Equation (17), in fact, shows that the viscosity of the mixture is obtained through the reference equations for the pure fluids. Information on mixture compounds is contained only in ψ^{mix}.

If pure-fluid viscosity equations are available for the components of a binary mixture, the model is said to be *closed* and the equation format changes from Eq. (12) to

$$\eta_{\mathrm{r}}^{\mathrm{mix}} (T_{\mathrm{r}}, P_{\mathrm{r}}, \bar{x}) = \eta_{\mathrm{r}}^{\mathrm{c1}} + \frac{\psi^{\mathrm{mix}} - \psi^{\mathrm{c1}}}{\psi^{\mathrm{c2}} - \psi^{\mathrm{c1}}} \left(\eta_{\mathrm{r}}^{\mathrm{c2}} - \eta_{\mathrm{r}}^{\mathrm{c1}}\right) \tag{18}$$

maintaining the same symbols, and superscripts c1, c2 refer to the first and second components of the mixture, respectively. If a pure-fluids viscosity equation is available only for a single mixture component, the model is said to be *semi-closed* and the equation format is similar to Eq. (18). The general case is referred to as *open*.

Apart from these particular conditions, the general aim is to propose a model that could be of general use with high accuracy for a wide range of thermodynamic conditions and for a large number of components. Going back to the previous discussion on the selection requirements and considering the results of a consistent number of tests with different reference fluids, it has been verified that the best results are obtained when *ethane* and *propane* are the reference fluid pair. Even though it could be argued that the ψ_i values of these two fluids are too close to allow a coherent extrapolation, some tests carried out changing the reference fluid pair showed that ethane and propane gave the wider range of applicability and accuracy to the model, primarily because of their accurate viscosity equations.

The sources for the reference fluid viscosity equations are Ref. [22] for ethane and Refs. [23, 24] for propane. For ethane a multiparameter equation of state in terms of the Helmholtz energy [25] was assumed, whereas for propane a MBWR32 equation of state [26] is applied.

According to the ranges of validity for the reference equations, the model is applicable at $0.32 \leqslant T_{\mathrm{r}} \leqslant 1.622$ and P_{r} up to 12.4, excluding a narrow range centered at the critical point with $0.99 \leqslant T_{\mathrm{r}} \leqslant 1.01$ and $0.95 \leqslant P_{\mathrm{r}} \leqslant 1.07$. A detailed analysis of the validity of the reference fluid equations is given in Ref. 5.

5. MIXTURE MODEL VALIDATION

The proposed viscosity model has been tested with experimental data, and the results are also compared with those from advanced literature models. The model is specifically dedicated to alkanes and haloalkanes making it coherent with the conformality approach on which it is based. On the other hand, the mixtures studied here are in these two families. Considering their molecular properties, such families are particularly interesting to study as the alkanes are nonpolar regular fluids, whereas the haloalkanes have different polarity levels and they are particularly difficult to model. Referring to the existing viscosity models, there are some differences. The Teja and Rice model [14] for pure fluids allows viscosity calculation only in the liquid phase and it does not take into account pressure effects, so that it is neither applicable for the vapor phase nor at high pressures, i.e., in supercritical and compressed liquid regions. The present model represents viscosity in the whole $P\rho T$ domain. In the proposed model the reference fluid viscosity equations are expressed in a $\eta = \eta\,(T, \rho)$ form and, making use of the equation of state, are then used in a direct $\eta = \eta\,(T, P)$ form. These are correlative equations being regressed on the available experimental data and their validity often ranges from the supercritical region to the triple point. This allows the range of the model to be extended on a corresponding ηPTx domain.

It is interesting to compare the obtained results with those of a similar model proposed by Okeson et al. [27, 28] setup on a similar structure and based on a four-parameter CS format [29, 30]. As the fourth parameter is related to the radius of gyration of the molecule, for some haloalkanes this quantity is not yet determined and in such cases the model has not been used. The performance of the viscosity model in the ECS format proposed by Ely and Hanley [1], Huber and Ely [2] and Klein et al. [16] is compared by applying the REFPROP software [31] which is claimed to be based upon the ECS model.

The present validation is limited by the availability and quality of data; the comparison of different data sets reveals large deviations and suggests that the experimental uncertainty of the available measurements is within 2–3%. As a consequence a model can be considered reliable if its prediction accuracy falls within the same range. On the other hand, the accuracy level claimed by the available pure fluid viscosity equations is not much better. Due to the limitation of the experimental data for the investigated mixtures, no preliminary statistical screening has been done on the quality of the data, and the results of the comparisons given here are subject to the experimental uncertainty. The model itself, as for any predictive or semipredictive model, does not allow data screening.

In the following, the mixture model is *completely predictive* since the interaction parameters are set to unity. The results of these comparisons are reported in Tables III–VI. The results are divided for alkane and haloalkane mixtures, and each family is subdivided into liquid and vapor phases.

5.1. Validation for Liquid Phase

The results for alkanes are reported in Table III. The selected mixtures include components for which the scaling parameters have been calculated and reported in Table I. Among the different types of mixtures

Table III. Validation for Alkanes in Liquid Phase and Comparisons with the Four-Parameter CS Model[a]

			Range		AAD (%)	AAD (%)	Max (%)	NPT > 5%	
Mixture	Model	Ref.	P (MPa)	T (K)	Four parameters	This model			NPT
C1 + C3	C	[32,33]	3–55	123–410	20.34	3.46	13.86	60	272
n-C5 + *n*-C6	O	[34]	0.1	298	10.07	0.92	1.63	0	11
n-C5 + *n*-C7	S	[34-36]	0.1	298–525	2.36	4.03	12.02	22	67
n-C6 + *n*-C7	S	[34,37]	0.1–71.74	303–323	13.25	2.54	8.55	13	64
n-C6 + *n*-C8	O	[34]	0.1	298	12.99	1.07	2.24	0	11
n-C7 + *n*-C8	S	[34]	0.1	298	9.85	1.65	2.51	0	11
n-C7 + *n*-C9	S	[34,37]	0.1–71.84	303–323	10.21	2.28	7.50	15	68
n-C8 + *n*-C9	O	[34]	0.1	298	11.87	3.48	4.69	0	11
n-C8 + *n*-C10	O	[34]	0.1	298	14.25	4.17	5.65	2	11
n-C9 + *n*-C10	O	[34]	0.1	298	12.38	3.87	4.72	0	11
n-C9 + *n*-C11	O	[34]	0.1	298	13.72	4.02	5.78	3	11
n-C10 + *n*-C11	O	[34]	0.1	298	12.41	3.23	4.02	0	11
n-C10 + *n*-C12	O	[34]	0.1	298	12.69	3.87	4.45	0	11
n-C11 + *n*-C12	O	[34]	0.1	298	14.07	4.11	5.59	3	11
n-C5 + *n*-C8	O	[34]	0.1	298	10.21	3.61	5.03	1	11
n-C5 + *n*-C10	O	[34]	0.1	298	13.43	4.62	8.21	8	11
n-C5 + *n*-C12	O	[34]	0.1	298	14.07	4.72	7.34	6	11
n-C6 + *n*-C9	O	[34]	0.1	298	11.31	3.98	6.03	3	11
n-C6 + *n*-C12	O	[34]	0.1	298	14.51	4.27	7.55	5	11
n-C7 + *n*-C10	S	[34]	0.1	298	7.32	1.26	4.24	0	11
n-C7 + *n*-C12	S	[34]	0.1	298	8.49	2.15	4.88	0	11
n-C8 + *n*-C12	O	[34]	0.1	298	11.37	3.62	7.18	5	11
n-C9 + *n*-C12	O	[34]	0.1	298	12.35	4.02	7.76	7	11
Overall					14.31	3.26	13.86	153	680

[a] Model: O = open, C = closed, S = semi-closed; AAD = absolute average deviation, Bias = bias, Max = maximum deviation; NPT = number of points.

Table IV. Validation for Haloalkanes in Liquid Phase and Comparison with the Four-Parameter CS Model and with ECS from REFPROP[a]

			Range		AAD (%)	AAD (%)	AAD (%)	Max (%)	NPT > 5%	
Mixture	Model	Ref.	P (MPa)	T (K)	Four parameters	REFPROP	This model			NPT
R125 + R134a	S	[38–40]	–	283–333		2.34	1.29	7.45	2	134
R152a + R134a	C	[38]	–	298–333		4.31	2.71	3.5	0	9
R152a + R125	S	[38]	–	233–333	17.46	4.21	5.95	9.31	11	19
R143a + R125	O	[38]	–	223–333		4.45	2.19	4.28	0	21
R143a + R134a	S	[38]	–	283–333	6.53	4.41	1.00	2.23	0	12
R22 + R142b	O	[41, 42]	–	201–352	4.96	3.42	3.60	17.74	20	73
R22 + R152a	S	[41]	–	242–352	8.97	4.69	2.96	9.13	5	30
R32 + R124	O	[39]	–	252–310		11.12	7.11	9.11	14	14
R32 + R125	O	[38]	–	223–333	14.46	5.31	2.57	15.4	2	21
R32 + R134a	S	[38, 40, 43]	–	252–333		1.90	2.07	5.1	1	169
R143a + R125 + R134a	S	[38]	–	273–333		8.46	1.10	4.21	0	7
R32 + R125 + R143a	O	[38]	–	223–333	20.94	13.75	18.1	24.85	12	12
R32 + R134a + R125	O	[40]	up to 3	245–340	20.94	0.89	2.30	4.31	15	96
Overall					13.71	3.03	2.71	24.8	82	617
Overall liquid (alkanes + haloalkanes)					14.14	3.03	2.99	24.8	235	1297

[a] Model: O = open, C = closed, S = semi-closed; AAD = absolute average deviation, Bias = bias, Max = maximum deviation; NPT = number of points.

Table V. Validation for Alkanes in Vapor Phase and Comparison with the Four-Parameter CS Model[a]

			Range		AAD (%)	AAD (%)	Max (%)	NPT > 5%	
Mixture	Model	Ref.	P (MPa)	T (K)	Four parameters	This model			NPT
C1 + C2	C	[21]	0.1	298–418	15.32	1.17	2.17	0	9
C1 + C3	C	[21, 33]	0.1–14	298–468	29.16	2.57	3.55	0	139
C1 + *n*-C4	C	[21]	0.1	298–468	26.8	4.24	6.04	6	15
C2 + C3	C	[21]	0.1	298–468	11.81	0.29	0.63	0	15
C2 + *n*-C4	C	[21]	0.1	298–468	20.24	1.27	2.84	0	15
C3 + *n*-C4	C	[21]	0.1	298–468	7.18	0.8	2.09	0	15
n-C5 + *n*-C7	S	[35]	–	443–524	7.47	14.38	26.74	27	33
Overall					22.52	3.91	26.74	33	241

[a] Model: O = open, C = closed, S = semi-closed; AAD = absolute average deviation, Bias = bias, Max = maximum deviation; NPT = number of points.

available, the selection criterion adopted here is referred to the number of the carbon atoms (n_{ca}) of the components: the first part of the validation includes mixtures having components with close n_{ca} as C1 + C3, *n*-C5 + *n*-C6, etc., while the remaining one presents components with high differences in the n_{ca} as *n*-C5 + *n*-C12. The REFPROP software does not include alkanes of higher n_{ca} so that the corresponding results are excluded from Tables III to VI. For alkanes the performance of the model depends more on the difference of n_{ca} for components than on the absolute n_{ca}. The error weakly increases moving from mixtures with components with close n_{ca} to those with relevant differences in n_{ca}. Interesting results are obtained with *closed* and *semi-closed* models, while higher errors are found for the four-parameter model [27, 28]. Regarding the results reported in Table IV for binary and ternary haloalkane mixtures, this model produces better results than the other two models selected for comparison and, in particular, with respect to REFPROP. The overall AAD for these systems is 2.71%, confirming the reliability of the predictive model. In fact the prediction accuracy looks very high, except for the cases of R32 + R124 and R32 + R125 + R143a. For these systems better results could be achieved by regressing the mixing rule interaction parameters, as will be pointed out later for the cases of azeotropic mixtures. An overall AAD of 2.99% is obtained for the liquid phase for alkanes and haloalkanes.

Table VI. Validation for Haloalkanes in Vapor Phase and Comparison with the Four Parameter CS Model and with ECS from REFPROP[a]

			Range		AAD (%)	AAD (%)	AAD (%)	Max (%)	NPT > 5%	
Mixture	Model	Ref.	P (MPa)	T (K)	Four parameters	REFPROP	This model			NPT
R143a + R125	O	[37]	0.1–2.4	226–401		1.36	5.59	11.95	23	46
R22 + R142b	O	[44]	0.1–11	243–473	9.1	3.2	2.55	15.83	125	971
R22 + R152a	S	[45,46]	0.1–0.7	273–323	3.46	1.2	0.50	1.87	0	260
R22 + C3	S	[46]	0.1	298–348	18.88	2.74	2.08	3.97	0	21
R32 + R125	O	[37]	0.1–3.1	221–397	6.63	1.56	6.24	12.73	29	54
R143a + R125 + R134a	S	[37]	0.1–2.7	269–393		1.20	5.22	15.5	14	41
R32 + R125 + R134a	O	[37]	0.1–2.5	236–399	9.6	2.10	2.56	9.6	6	43
Overall					8.08	2.62	2.48	15.8	197	1436
Overall vapor (alkanes+haloalkanes)					10.26	2.62	2.68	26.7	230	1677

[a] Model: O = open, C = closed, S = semi-closed; AAD = absolute average deviation, Bias = bias, Max = maximum deviation; NPT = number of points.

5.2. Validation for Vapor Phase

The analysis of the results for vapor phase alkanes, Table V, shows good performance of the model except for the *n*-C5 + *n*-C7 mixture for which a significant deviation is found. For haloalkanes the performance is comparable with the results in Table VI, and the overall AAD of 2.48% is within the claimed experimental uncertainty and is comparable with the performances of the pure fluid equations. Excluding the R32 + R125 and R143a + R125 + R134a systems, the results obtained by the proposed model in the *predictive* mode are quite similar to those produced by the REFPROP calculation, which is based on a *correlative* format. In fact, considering together alkanes and haloalkanes, an overall AAD of 2.68% is obtained for the vapor phase. However, due to the limited number of experimental sources and data available, general conclusions cannot be drawn.

5.3. Validation for Multicomponent Systems

The model has been furthermore validated for multicomponent systems; three quaternary mixtures and a quinary mixture of hydrocarbons have been studied. Viscosity mixture data for systems with more than three components were not found for haloalkanes. To better exploit the conformality of the components of the studied mixtures, a model specific for alkanes has been setup for this case in which *n*-C4 and *n*-C7 have been selected as reference fluids with the scaling parameters determined with respect to *n*-C4. For the corresponding pure fluid equations, the reference source is Huber [47], whereas the data for validation come from Wu et al. [48].

The results reported in Table VII show that the model performance is very accurate, in particular for those mixtures having *n*-C7 as component.

Table VII. Validation for Multicomponent Alkane Mixtures in Liquid Phase; data from Ref. [48][a]

Mixture	AAD (%)	Bias (%)	Max (%)	NPT
n-C7 + *n*-C8 + *n*-C11 + *n*-C13	0.87	−0.79	3.59	28
n-C8 + *n*-C10 + *n*-C11 + *n*-C15	1.86	−1.86	2.42	10
n-C8 + *n*-C11 + *n*-C13 + *n*-C15	1.70	−1.70	2.22	10
n-C7 + *n*-C8 + *n*-C11 + *n*-C13 + *n*-C15	1.61	−1.61	2.03	7
n-C7 + *n*-C8 + *n*-C11 + *n*-C13	0.87	−0.79	3.59	28
Overall	1.15	−1.09	3.59	83

[a] AAD = absolute average deviation, Bias = bias, Max = maximum deviation; NPT = number of points.

As previously observed for *closed* or *semi-closed* systems, the calculation of the pure component properties highly improves the prediction accuracy.

5.4. Validation for Azeotropic Mixtures

The model has also been validated with liquid viscosity data of the two irregular mixtures R32 + R290 and R134a + R290 presenting definite azeotropic behavior. For this type of systems the model can be effective only by including the interaction coefficients α_{ij} and β_{ij} in the mixing rules, Eqs. (7)–(11). In order to find the minimum amount of data needed for fitting the interaction coefficients, different data sets have been used leading to different α_{ij}, β_{ij} values and finally to different model accuracy.

Data spread on different regions of variable domains have been used, to explore the more effective ones. In this way, if the viscosity of azeotropic mixtures is to be modeled, a reliable indication about where and how many data to measure is provided. Results are reported in Tables VIII and IX, and the experimental data used for comparison are from Laesecke et al. [40].

A limited number of experimental points used to fit the two interaction parameters enables one to obtain a large improvement in the results. Besides, the tuning of the mixing rules seems to be ineffective using data at the same T and different x, but it is more effective using several T at a constant composition. The correction is then needed only for temperature and not for composition, confirming in this case the high effectiveness of the mixing rules.

For the R32 + R290 mixture, the interaction parameters referred to the case in bold type in Table VIII are: $\alpha_{ij} = 1.029699$, $\beta_{ij} = 0.887436$. Similarly, for the R134a + R290 mixture the interaction parameters

Table VIII. Model Validation for the Azeotropic Mixture R32 + R290, Data from Ref. [40][a]

NPT = 128 Regression procedure	AAD (%)	Bias (%)	Max (%)	NPT for regression
Predictive	22.60	22.60	36.39	0
Same x, two extreme T of the exp. range	1.15	−1.14	3.20	2
On data at the same x and several T	**0.56**	**−0.20**	**2.21**	**9**
On data at the same T and two x	1.77	−1.73	6.23	2
On data at several x and several T	0.54	−0.06	2.04	15

[a] AAD = absolute average deviation, Bias = bias, Max = maximum deviation; NPT = number of points.

referred to the case in bold type in Table IX are: $\alpha_{ij} = 1.517536$, $\beta_{ij} = 0.949145$.

Figures 3 and 4 report the deviations as a function of temperature of both the present model and of REFPROP [31] with respect to the same data for the R32 + R290 and the R134a + R290 mixtures [40], respectively. For comparison the REFPROP [31] prediction accuracies for these two azeotropic mixtures are AAD = 1.58 % for R32 + R290 and 4.68 % for R134a + R290. An evident increase in prediction accuracy is shown by the proposed model.

Table IX. Model Validation for the Azeotropic Mixture R134a + R290, Data from Ref. [40][a]

NPT = 161 Regression procedure	AAD (%)	Bias (%)	Max (%)	NPT for regression
Predictive	30.90	30.90	32.40	0
Same *x*, two extreme *T* of the exp. range	**1.15**	**0.22**	**3.77**	**2**
On data at the same *x* and several *T*	1.66	−1.33	5.08	7
On data at the same *T* and two *x*	26.45	−26.45	84.31	2
On data at several *x* and several *T*	1.16	0.07	3.86	13

[a] AAD = absolute average deviation, Bias = bias, Max = maximum deviation; NPT = number of points.

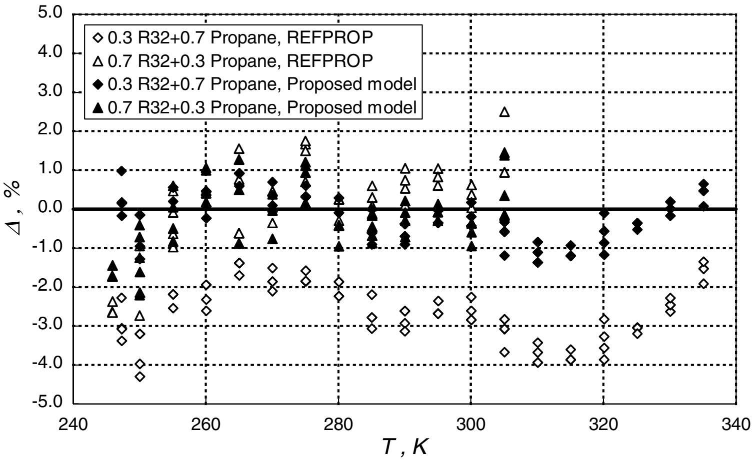


Fig. 3. Deviations of both the present model and of REFPROP [31] with respect to data from Ref. [40] for the azeotropic mixture R32 + R290.

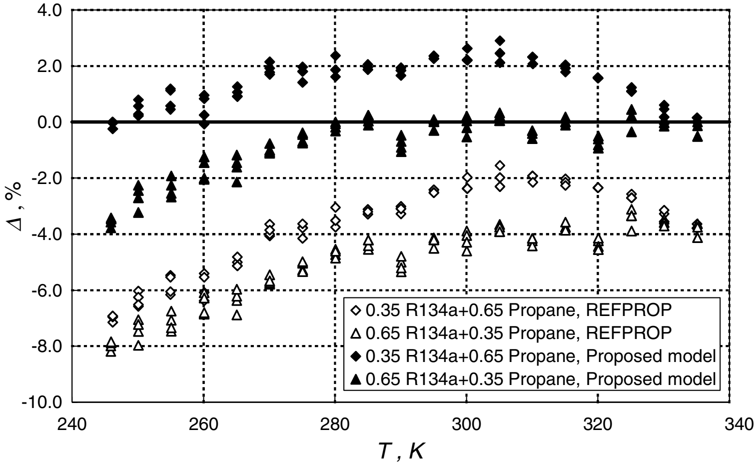


Fig. 4. Deviations of both the present model and of REFPROP [31] with respect to data from Ref. [40] for the azeotropic mixture R134a + R290.

5.5. Comparison with a Recent Model.

A significant test is presented in this section comparing the obtained results for some mixtures with those obtained by applying a viscosity model recently published by Assael et al. [12]. The model is based on a theoretical scheme of Vesovic and Wakeham and modified by Dymond and Assael making use of the hard-sphere theory specifically to predict the viscosity of mixtures in the liquid phase. This paper [12] includes some mixtures also examined in the present work. In particular, the results for the alkane mixture *n*-C6 + *n*-C7 and those of the haloalkane mixture, R125 + R134a, are considered here. Referring to the first mixture, on a total of 35 experimental points, the AAD is 9.46%, while for the second one the AAD is 4.44% on 15 points. The results reported in Tables III and IV are significantly better, as the AAD values are 2.54% on 64 points for the *n*-C6 + *n*-C7 mixture and 1.29% on 134 points for R125 + R134a. These results are calculated in a completely predictive mode, while the model from the cited paper [12] requires the molar density and the viscosity of the pure fluids in addition to the molar density of the mixture at the temperature of interest. However, the cited model has been tested on a wide range of mixtures consisting of hydrocarbons, alcohols, and their combinations with hydrocarbons and halogenated alkanes, and the results have consistently demonstrated good agreement with the experiment. On the other hand, the proposed model demonstrates better accuracy when specifically dedicated to a more limited group of fluids.

6. CONCLUSIONS

A predictive model to calculate the viscosity of mixtures of alkanes and halogenated alkanes is proposed in this work. The model investigates the potential of CS methods and exploits an original approach based on a *conformality analysis* of the viscosity surfaces of pure fluids. This allows the determination of a *new scaling parameter* specific for viscosity, for a model in a three-parameter CS format. Two pure-fluid viscosity equations with a wide ηPT validity domain are selected for the fluids used as references, and the model is tested on both liquid and vapor conditions. The model is extended to mixtures following the *one-fluid-model* approach through mixing rules. Considering that no information on the mixture of interest is required and that only a single parameter for each component is needed, the proposed model has a completely predictive character.

A large number of mixtures of *n*-alkanes, from C1 to *n*-C12, and halogenated alkanes including R134a, R125, R152a, R143a, R22, R142b, R32, and R124 have been investigated. The overall accuracy on both families, expressed in terms of AAD (%), is within 2.68% for the vapor phase on a total of 1677 points to 2.99% in liquid conditions on 1297 points. Excellent results are reached for multicomponent systems of heavy *n*-alkanes, while a decrease in performance is observed for ternary haloalkane systems. The model has also been validated against strongly azeotropic mixtures, such as R32 + R290 and R134a + R290. The results obtained in the predictive mode are not satisfactory, but by fitting the interaction parameters on a very limited number of experimental data, higher accuracies are reached. The comparison with a recently published method confirms the effectiveness of the mixing rules and the potential of this CS approach.

Considering the predictive nature of the model and that no preliminary screening has been done on the data, the obtained results demonstrate the high potential of the CS predictions for transport properties and make this method promising for the prediction of thermophysical properties.

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