© 2008 The Chemical Society of Japan Bull. Chem. Soc. Jpn. Vol. 81, No. 10, 1219–1229 (2008) 1219

Assessment of the Effect of Mixing Rules on Transport Properties of Gas Mixtures

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The purpose of this paper is to examine the effect of six different mixing rules on the calculated transport properties including viscosities and thermal conductivities of some binary and ternary gas mixtures. These properties are calculated using pair potential energies of the systems obtained from the inversion procedure. The Chapman–Enskog theory and Schreiber's method are employed to calculate viscosity and thermal conductivity of different mixtures, respectively. Different mixing rules do not behave the same in predicting the two aforementioned properties. The Fit (MADAR-2) mixing rule gives rise to more acceptable viscosity values, while the Halgren-HHG rule stands over other mixing rules in predicting thermal conductivity. It is found that, when the mixture components are similar in size, different mixing rules often do not change the errors in calculated properties more than ±1%. However, as the size similarity decreases, the effect of applied mixing rules becomes more important. In this case, different mixing rules are able to change the errors in calculations at most ±3.5%. The collision diameters (σ) of our studied mixture components, vary from 2.641 Å for He, to 5.26 Å for R125. The energy scaling parameters (ε) of mixture components range from 10.956 K for He to 475.76 K for C_4H_{10}.

Non ideal behavior of gases is largely determined by the interactions between pairs of gas molecules which can be described by intermolecular potentials. In a gaseous mixture, there will also be interactions between non-identical molecules. The unlike interactions are accounted for using mixing rules.

There is some ambiguity in distinguishing between the terms "mixing" and "combining" rules. They are used interchangeably in the literature. However, Wei and Sadus[1] used the term "mixing rule" to indicate the expressions used to obtain parameters for the van der Waals one fluid theory, while the term "combining rule" was used for mathematical expressions used to obtain cross interaction values from pure component values.

The distance between particles i and j (σ_{ij}), scales the length of the interaction, and (ε_{ij}), scales the well depth of the potential. Interaction between dissimilar particles requires the generation of cross term parameters for σ and ε. To estimate the potential between non-identical molecules, the Lorentz–Berthelot mixing rules are frequently used to mix the parameters from the systems for the two pairs of identical molecules. This mixing rule uses an arithmetic rule for the collision diameter (Lorentz rule) and a geometric mean for the well depth (Berthelot rule).

In this section we give an introduction to mixing rules, and the constraints placed upon them and also introduce the mixing rules which we have examined their effect on viscosities and thermal conductivities of some representative mixtures.

For N types of interaction sites, one needs to define $N(N+1)/2$ interaction parameter sets. This is a huge number and reduces the versatility of pure site interaction parameters. Instead of specifying the off-diagonal terms in such parameter sets, the common practice is to use mixing (combination) rules which allow the use of pure site parameters only. This requires specifying only N parameter sets. In matrix form, the following array depicts these concepts for an N site case, where bold face denotes the vector of parameter sets involved. The boxed elements are the elements that require specification when using mixing rules.

$$\begin{bmatrix} \boxed{a_{1,1}} & a_{1,2} & \cdots & a_{1,N-1} & a_{1,N} \\ a_{2,1} & \boxed{\ddots} & \cdots & a_{2,N-1} & a_{2,N} \\ \vdots & \ddots & \boxed{\cdots} & \ddots & \vdots \\ a_{N-1,1} & \ddots & \cdots & \boxed{\ddots} & a_{N-1,N} \\ a_{N,1} & a_{N,2} & \cdots & a_{N,N-1} & \boxed{a_{N,N}} \end{bmatrix} \qquad (1)$$

With this in mind, the problem is posed as: consider a system C composed of N components $A_1 \ldots A_N$. Can a property c of the system be predicted from knowledge of the pure constituent properties $\mathbf{a}$, where $\mathbf{a}$ is the vector of pure component properties ($\mathbf{b}$, $\mathbf{c}$, ...)? The mathematical relationship corresponding to the posed problem is called a mixing rule. Mixing rules can be divided either on some theoretical background or purely empirical correlation of experimental data.[2]

There are four rigorous mathematical constraints that each mixing rule should satisfy in order to be useful in predicting mixture parameters from knowledge of those for the pure components.

1. Symmetry

$$f(\mathbf{a}) = f(\mathbf{a}^T) \qquad (2)$$

Published on the web October 10, 2008; doi:10.1246/bcsj.81.1219

is essential, to reduce the number of parameter sets involved. In principle, the method proposed can be used without this constraint. However, it will require specifying $2N$ parameter sets instead of N sets.

2. The function is scalable or invariant with uniform scaling of **a**, and **c**. This is important for the model to be useful among different systems of units,

$$sc = f(s\mathbf{a}) \tag{3}$$

3. Identity relationship for a mixture composed of the same components should predict the properties of the pure component,[3]

$$c = f(\mathbf{a}_{\text{pure}}) = \|\mathbf{a}\| = a \tag{4}$$

4. If composition dependence is to be included, avoid the Michelsen–Kistenmacher syndrome. This implies that the rule must be invariant to the division of a component into identical subcomponents.[4]

In addition to these requirements, one can think of other desirable features the mixing rule should possess. Simplicity of the mixing rule is the most demanding aspect. Computational efficiency and the lowest number of adjustable parameters (if any) are other desirable features.[2]

Theoretical

In this work, we study six different mixing rules: Lorentz–Berthelot, Halgren HHG, Tang–Toennies, Waldman–Hagler, Functional (MADAR-1), and Fit (MADAR-2). The last two rules were developed by Al-Matar and Rockstraw[2] based on a certain weighting matrix approach for devising mixing rules. The Tang–Toennies rules belong to theoretically developed rules, while all other rules are empirical expressions developed to match experimental data with the prediction from the rules. The mathematical forms of the rules implemented in this research are given below.

Lorentz–Berthelot. These rules are the most widely used.[5,6] An arithmetic average is used for the collision diameter, while a geometric average is used for the well depth.

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{5}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{6}$$

Halgren HHG. These rules implement a weighted average of the arithmetic-mean rule for σ; the weight factor being the square of the value.[7] For ε, Halgren HHG applies a harmonic mean of the harmonic and geometric mean values.[7]

$$\sigma_{ij} = \frac{\sigma_{ii}^3 + \sigma_{jj}^3}{\sigma_{ii}^2 + \sigma_{jj}^2} \tag{7}$$

$$\varepsilon_{ij} = \frac{4\varepsilon_{ii}\varepsilon_{jj}}{(\varepsilon_{ii}^{1/2} + \varepsilon_{jj}^{1/2})^2} \tag{8}$$

Tang–Toennies.[8] These rules are based on some quantum mechanical derivation and are the most successful equation among the group of theoretical rules. The problem with such an approach is the incorporation of additional parameter sets (e.g. polarizability, ionization potentials, or dispersion force coefficients). This is contradictory to the purpose behind introducing mixing rules. Mixing rules are introduced to reduce the number of parameter sets in any force field, while theoretical rules introduce more parameters and some of them are not easily determined.

$$\sigma_{ij}^6 = \frac{(0.5(\varepsilon_{ii}^{1/13}\sigma_{ii}^{12/13} + \varepsilon_{jj}^{1/13}\sigma_{jj}^{12/13}))^{13}}{(\varepsilon_{ii}\varepsilon_{jj})^{1/2}(\sigma_{ii}\sigma_{jj})^3} \tag{9}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}\left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6}\right)\frac{C_{6,ij}}{(C_{6,ii}C_{6,jj})^{1/2}} \tag{10}$$

Where $C_{6,ii}$ and $C_{6,jj}$, are dispersion coefficients of components i and j, respectively, and $C_{6,ij}$, is the dispersion coefficient for binary mixture ij.

Waldman–Hagler. This rule utilizes a sixth power mean for collision diameter and a simplified form of the reduced sixth dispersion coefficient for the well depth.[3]

$$\sigma_{ij} = \left(\frac{\sigma_{ii}^6 + \sigma_{jj}^6}{2}\right)^{1/6} \tag{11}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}\left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6}\right) \tag{12}$$

Functional (MADAR-1). This rule is derived based on extensive functional analysis of the behavior of the available experimental data.[2,9] It takes the form:

$$\sigma_{ij} = \frac{1}{3}\sum_{L=0}^{2}\left(\frac{0.25(\sigma_{ii}^3 + \sigma_{jj}^3)^2}{\sigma_{ii}^L\sigma_{jj}^L}\right)^{\frac{1}{6-2L}} \tag{13}$$

$$\varepsilon_{ij} = 3(\varepsilon_{ii}\varepsilon_{jj})^{1/2}\frac{\sigma_{ii}^3\sigma_{jj}^3}{\displaystyle\sum_{L=0}^{2}\left(\frac{0.25(\sigma_{ii}^3 + \sigma_{jj}^3)^2}{\sigma_{ii}^L\sigma_{jj}^L}\right)^{\frac{6}{6-2L}}} \tag{14}$$

Fit (MADAR-2). A least-squares analysis was carried out for both σ and ε to determine the weight factors matrix[2,9] for the fit form. The data set of Kestin and co-workers[10,11] was used throughout. The power was fixed to the sixth power for theoretical considerations; however, it can be treated as an adjustable parameter. The final equations called fit (MADAR-2) take the form:

$$\sigma_{ij} = \left(\frac{0.5640\sigma_{ii}^6 + 0.9464\sigma_{ii}^3\sigma_{jj}^3 + 0.4896\sigma_{jj}^6}{2}\right)^{1/6} \tag{15}$$

$$\varepsilon_{ij} = \left(\frac{0.0799\varepsilon_{ii} + 1.912939769(\varepsilon_{ii}\varepsilon_{jj})^{1/2} + 0.0071\varepsilon_{jj}}{2}\right) \times \left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6}\right) \tag{16}$$

Where subscript i, represents the lighter component and subscript j, the heavier component of the i–j pair.

The main objective of this work is to assess the effect of these six mixing rules on the accuracies of predicted transport properties, including viscosities and thermal conductivities of some binary and ternary dilute gas mixtures. We have selected wide varieties of mixtures consisting of: Ar–H_2 mixture as representative of atom–diatom mixture, binary alkane mixtures of methane–ethane and propane–butane, ternary equimolar ethane–propane–butane mixture as representatives of non-polar polyatomic mixtures and refrigerant mixtures of R125 (pentafluoroethane)–R134a (1,1,1,2-tetrafluoroethane), R507A [50 wt% R143a (1,1,1-trifluoroethane) and 50 wt% R125], R404A (52 wt% R143a, 44 wt% R125, and 4 wt% R134a), and R32 (difluoromethane)–R125–R134a as representatives of slightly polar mixtures. Also we have studied the effect of using different mixing rules on the calculated viscosities of He–CO_2 and H_2–C_2H_6 binary mixtures. We chose these two mixtures because of the greater difference between the sizes of their components.

Results and Discussion

There have not been many studies to assess the effect of mixing rules on the accuracies of the predicted transport properties in the literature, so this study can provide a logical framework for selecting the most suitable mixing rules, based on an objective criteria.

In our previous works,[12–16] we employed a corresponding states correlation for functional viscosity collision integrals to establish pair potential energies of several mixtures, by the use of a two-iterative inversion procedure. Details of this method have been outlined elsewhere.[17]

We used the kinetic theory expressions based on the Chapman–Enskog[18,19] solution of the Boltzmann equation to calculate viscosities and the method proposed by Schreiber et al.,[20] to evaluate the thermal conductivities of studied mixtures. In the next section the necessary formulas will be presented.

To calculate mixture transport properties we need to know binary potential parameters σ_{12} and ε_{12}, in terms of σ and ε of pure components. Mixing (combining) rules determine how the cross coefficients σ_{12} and ε_{12} are calculated. Maitland et al.[21] provides a good review of the mixing rules literature prior to 1981. In the present work more recent rules including those of Tang and Toennies,[22] Halgren,[7] Waldman and Hagler,[3] and also Al-Matar and Rockstraw[2] have been applied to check the effect of mixing rules on transport properties.

The common belief is that the mixing rules do not appreciably affect the outcome of a calculation, so there have not been many studies to assess the effect of mixing rules to the accuracy of thermophysical properties. The present work indicates that the results are slightly in favor of the Halgren-HHG mixing rule[7] for thermal conductivities and Fit (MADAR-2)[2] mixing rule, for viscosities of studied mixtures. On the other hand, this assessment shows the superiority of the Lorentz–Berthelot mixing rule in calculation of viscosities when the mixture components differ considerably in size.

Applicable Formulas for Transport Properties. Viscosity: The kinetic theory expression for the viscosity, in terms of collision integrals, for a mixture of gases, is given below:[23]

$$\eta_{\text{mix}} = -\frac{\begin{vmatrix} H_{11} & H_{12} & \cdots & H_{1\nu} & x_1 \\ H_{21} & H_{22} & \cdots & H_{2\nu} & x_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ H_{\nu 1} & H_{\nu 2} & \cdots & H_{\nu\nu} & x_\nu \\ x_1 & x_2 & \cdots & x_\nu & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & H_{12} & \cdots & H_{1\nu} \\ H_{21} & H_{22} & \cdots & H_{2\nu} \\ \vdots & \vdots & \ddots & \vdots \\ H_{\nu 1} & H_{\nu 2} & \cdots & H_{\nu\nu} \end{vmatrix}} \tag{17}$$

$$H_{ii} = \frac{x_i{}^2}{\eta_i} + \sum_{\substack{k=1\\k\neq i}}^{\nu} \frac{2x_ix_k}{\eta_{ik}} \frac{m_im_k}{(m_k+m_i)^2}\left(\frac{5}{3A_{ik}{}^*}+\frac{m_k}{m_i}\right) \tag{18}$$

$$H_{ij}(i\neq j) = -\frac{2x_ix_j}{\eta_{ij}}\frac{m_im_j}{(m_i+m_j)^2}\left(\frac{5}{3A_{ik}{}^*}-1\right) \tag{19}$$

$$\eta_{ij} = \frac{5}{16}\left[\left(\frac{2m_im_j}{m_i+m_j}\right)\frac{kT}{\pi}\right]^{1/2}\frac{1}{\sigma_{ij}{}^2\Omega_{ij}{}^{*(2,2)}(T_{ij}{}^*)} \tag{20}$$

Where $\Omega^{*(2,2)}$ stands for the collision integral defined in Ref. 17. $A_{ij}{}^*$ is the ratio of the collision integrals,[17] x is the mole fraction of components, and η_{ij} is the interaction viscosity. In the above equations, subscript i, represents the heavier component and subscript j, the lighter component of the i–j pair.

Thermal Conductivity: Due to the fact that the internal degrees of freedom of polyatomic molecules are involved in transporting energy in gases, and on the other hand, in the basic development of the Chapman–Enskog theory, only binary elastic collisions between the molecules are considered and also molecules are taken to be without internal degrees of freedom, thus this theory cannot be applied to predict thermal conductivity.

To calculate the thermal conductivity of the present mixtures we employed the method proposed by Schreiber et al.[20] for polyatomic dilute gas mixtures. This method will be introduced in the next section. This scheme has already been tested against the available experimental data for some non-polar mixtures.[24]

Theory of Thermal Conductivity: The thermal conductivity of a multi-component polyatomic gas mixture at zero density can be expressed in a form analogous to that for a mixture consisting of monatomic species:[20]

$$\lambda = -\begin{vmatrix} L_{11} & \cdots & L_{1n} & x_1 \\ \vdots & \cdots & \vdots & \vdots \\ L_{n1} & \cdots & L_{nn} & x_n \\ x_1 & \cdots & x_n & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11} & \cdots & L_{1n} \\ \vdots & \cdots & \vdots \\ L_{n1} & \cdots & L_{nn} \end{vmatrix} \tag{21}$$

Where x_i is the mole fraction of species i and the symbol λ indicates the full formal first-order kinetic theory result obtained by means of expansion in Thijsse basis vectors.[25] The resulting expressions for the elements of the determinants, L_{ij}, were first derived by Ross et al.[26] which were complicated functions of the effective cross-sections and had little value for practical evaluation of thermal conductivity.

For the sake of simplicity, all quantities that enter the expressions for the elements L_{ij} in eq 21 were replaced by their spherical limits based on the results obtained for an atom–molecule mixture.[27] Following the application of Thijsse and spherical approximations to the full results, Schreiber et al.[20] derived the relevant determinant elements, L_{ij}, as:

$$\begin{aligned} L_{qq} = \frac{x_q^2}{\lambda_q} + \sum_{\mu\neq q}\frac{25x_qx_\mu}{8A_{q\mu}^*\lambda_{q\mu}}\left(\frac{R}{C_{pq}^0}\right)^2\Bigg[\frac{25}{4}y_\mu^4 + \frac{15}{2}y_q^4 \\ - 3y_\mu^4B_{q\mu}^* + 4y_q^2y_\mu^2A_{q\mu}^* + \left(\frac{C_{pq}^0}{R}-2.5\right)\Bigg] \end{aligned} \tag{22}$$

$$L_{qq'} = -\frac{25x_q x_{q'} y_q^2 y_{q'}^2}{8A^*_{qq'}\lambda_{qq'}}\left(\frac{R}{C^0_{pq}}\right)\left(\frac{R}{C^0_{pq'}}\right) \times \left[\frac{55}{4} - 3B^*_{qq'} - 4A^*_{qq'}\right] \tag{23}$$

where λ_q is the thermal conductivity of pure molecular species q, $\lambda_{qq'}$ is the interaction thermal conductivity, C^0_{pq} is the ideal-gas isobaric heat capacity of q, R is the gas constant, and the quantities A^* and B^* are ratios of effective cross-sections.[17] In addition y_q is the mass ratio of species q, given by:

$$y_q^2 = \frac{M_q}{(M_q + M_{q'})} \tag{24}$$

where M_q is the relative molecular weight of species q. The interaction thermal conductivity can be related to the more readily available viscosity, $\eta_{qq'}$,

$$\lambda_{qq'} = \frac{15}{8}R\frac{(M_q + M_{q'})}{M_q M_{q'}}\eta_{qq'} \tag{25}$$

Evaluation of the thermal conductivity of a multi-component polyatomic gas mixture thus requires knowledge of the thermal conductivity and the isobaric heat capacity of each of the pure species. This information is readily available for a large number of fluids as a function of temperature, either in terms of correlations or directly from experimental information. Furthermore, three binary interaction parameters, namely, $\eta_{qq'}$, A^*, and B^*, are also required as a function of temperature. In the present work, these quantities have been computed for all studied mixtures, from the calculated interaction viscosity and collision integral ratios obtained from the inversion method.[12–16]

As was mentioned before, in our recent works, an iterative inversion procedure has been employed to define the intermolecular pair interaction potential energies of some mixtures from corresponding states correlation for viscosity.[12–16] The inversion procedure is of considerable importance to obtain nonparametric interaction potential energy and transport properties. This scheme relives us of the variation of the selected multi-parameter analytic equation parameters for the pair potential function so as to optimize the fit to a wide range of thermophysical data of a material.[17]

In the second stage, using the inverted pair potential energies along with the Chapman–Enskog[18,19] version of the kinetic theory of gases and the method proposed by Schreiber et al.,[20] respectively, viscosities and thermal conductivities of our studied mixtures with acceptable accuracies have been predicted.[12–16]

In this paper in order to examine the effect of different mixing rules on the predicted values of viscosities and thermal conductivities, we chose some of our previously studied binary and ternary mixtures. These mixtures consist of:

(1) Ar–H_2 mixture as atom–diatom candidate.

(2) Binary alkane mixtures: methane–ethane and propane–butane.

(3) Ternary alkane mixture: ethane–propane–butane as candidates of non polar polyatomic mixtures.

(4) Binary refrigerant mixtures: R125–R134a in two different mole fractions and R507A: 50 wt % R125 and 50 wt % R143a, and also,

(5) Ternary refrigerant mixtures: R407C: 23 wt % R32, 25 wt % R125, and 52 wt % R134a and R404A: 44 wt % R125, 4 wt % R134a, and 52 wt % R143a as candidates of slightly polar mixtures.

In addition, we selected two mixtures with greater difference between the sizes of their components:

(6) He–CO_2 and H_2–C_2H_6 binary mixtures.

It is obvious that in order to calculate the binary potential parameters for each mixture, we need to know the scaling parameters, σ and ε for pure components.

We took pure component parameters ε and σ for Ar, He, CH_4, C_2H_6, and CO_2, from Ref. 28, for H_2 from Ref. 29, for C_3H_8 and C_4H_{10} from Najafi et al.,[30] for R134a from Ref. 31, and for the remaining three refrigerants (R125, R32, and R143a), we calculated the values of σ from the following equation:[32]

$$\sigma = 0.809(V_c)^{1/3} \tag{26}$$

Where V_c is the critical volume. The values of ε were evaluated using a corresponding states correlation for $\Omega^{*(2,2)}$ given in Ref. 21 in conjunction with a nonlinear least-squares method. Table 1 shows these parameters for the pure components.

Table 1. Collision Diameters and Well Depths for the Pure Components, Comprising Our Studied Mixtures

Pure component	σ/Å	(ε/k_B)/K
Ar	3.35	141.5
H_2	2.97	30.41
CH_4	3.721	161.4
C_2H_6	4.371	241.9
C_3H_8	4.721	353.35
C_4H_{10}	4.949	475.76
R125	5.26	235.85
R134a	5.076	283
R143a	4.69123	352.87
R32	4.02002	314.876
He	2.641	10.956
CO_2	3.769	245.3

In Tables 2–4 we have shown the calculated values of collision diameters and well depths of binary mixtures via six different mixing rules. In the case of ternary mixtures, we can assume that any three body interaction is approximately the sum of three two body interactions between the components comprising the mixture. Tables 5–7 contain the binary potential parameters of two body interactions for the three studied ternary mixtures.

As the Tables 2–7 indicate, the Lorentz–Berthelot mixing rule consistently underestimates the collision diameter and overestimate the well depth. The underestimation of the collision diameter is proportional to the difference in size between the binary components.

A close look at the values of σ_{ij} and ε_{ij} reveals that all mixing rules give almost the same results for potential parameters, when the two mixture components are similar in size. For example, Table 6 shows that the σ_{ij} and ε_{ij} values of R134a–R125 binary mixture, calculated from all mixing rules, are almost the same which is due to the size similarity of R134a and R125. In contrast, in the case of R32–R125 and R32–R134a, having less size similarity leads to more different σ_{ij} and ε_{ij}

Table 2. Collision Diameters and Well Depths, Using Different Mixing Rules for the Ar–H_2 Methane–Ethane and Propane–Butane Binary Mixtures

Mixing rule	Mixture					
	Ar–H_2		CH_4–C_2H_6		C_3H_8–C_4H_{10}	
	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K
Lorentz–Berthelot	3.16	65.5974	4.046	197.59	4.8350	410.0119
Halgren-HHG	3.18277	56.7858	4.0979	195.5839	4.8404	407.7529
Tang–Toennies	3.19946	60.2318	4.0683	187.4947	4.8394	407.0838
Waldman–Hagler	3.18803	61.5393	4.1092	176.5904	4.8417	405.9415
Functional (MADAR-1)	3.18577	61.7863	4.1049	177.5212	4.8410	406.2662
Fit (MADAR-2)	3.17926	65.3360	4.0858	184.2441	4.8421	408.114

Table 3. Collision Diameters and Well Depths, Using Different Mixing Rules for the R125–R134a and R507A (50 wt %R125–50 wt %R143a) Binary Mixtures

Mixing rule	Mixture			
	R125–R134a mixture		R507A mixture	
	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K
Lorentz–Berthelot	5.168	258.35	4.976	288.486
Halgren-HHG	5.171	257.82	5.008	285.579
Tang–Toennies	5.168	258.11	4.975	285.88
Waldman–Hagler	5.1721	256.884	5.0156	272.27
Functional (MADAR-1)	5.1717	257.0038	5.012	273.303
Fit (MADAR-2)	5.1732	255.7448	5.003	274.426

Table 4. Collision Diameters and Well Depths, Using Different Mixing Rules for He–CO_2 and H_2–C_2H_6 Binary Mixtures

Mixing rule	Mixture			
	He–CO_2 mixture		H_2–C_2H_6 mixture	
	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K
Lorentz–Berthelot	3.205	54.841	3.670	85.768
Halgren-HHG	3.397	29.866	3.928	66.295
Tang–Toennies	3.438	30.934	3.870	55.887
Waldman–Hagler	3.421	31.897	3.955	48.991
Functional (MADAR-1)	3.431	30.625	3.976	46.031
Fit (MADAR-2)	3.328	43.152	3.833	63.362

Table 5. Collision Diameters and Well Depths, Using Different Mixing Rules for the Three Binary Interactions between the Components of Ethane–Propane–Butane Ternary Mixture

Mixing rule	Mixture					
	Ethane–Propane		Ethane–Butane		Propane–Butane	
	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K
Lorentz–Berthelot	4.546	292.3617	4.66	339.2438	4.835	410.0119
Halgren-HHG	4.5594	289.7535	4.6957	329.7254	4.8404	407.7529
Tang–Toennies	4.555	287.6276	4.6861	324.2874	4.8394	407.0838
Waldman–Hagler	4.5627	284.7255	4.7039	316.9866	4.8417	405.9415
Functional (MADAR-1)	4.5612	285.29	4.70038	318.3104	4.8411	406.2662
Fit (MADAR-2)	4.5597	288.0424	4.6899	327.5789	4.8421	408.114

Table 6. Collision Diameters and Well Depths, Using Different Mixing Rules for the Three Binary Interactions between the Components of R407C (23 wt % R32, 25 wt % R125, and 52 wt % R134a) Ternary Mixture

Mixing rule	Mixture					
	R32–R125		R32–R134a		R125–R134a	
	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K	σ/Å	(ε/k_B)/K
Lorentz–Berthelot	4.64	269.946	4.548	295.701	5.168	258.352
Halgren-HHG	4.803	268.719	4.669	295.558	5.1713	257.816
Tang–Toennies	4.6631	248.236	4.571	275.56	5.1677	258.202
Waldman–Hagler	4.8302	200.962	4.6915	235.627	5.1721	256.885
Functional (MADAR-1)	4.8277	200.051	4.6806	236.063	5.1717	257.004
Fit (MADAR-2)	4.7496	221.31	4.6321	253.96	5.1732	255.745

values when various mixing rules are employed.

Equations 16–19, derived from the Chapman–Enskog version of the kinetic theory, together with the calculated collision integrals[12–16] obtained from the inverted potential energies, and also six aforementioned mixing rules were employed to compute viscosities of our studied mixtures. Because of the large amount of computations, here we only report the final results and discuss the effect of mixing rules on them.

The viscosity values of an equimolar Ar–H_2 mixture in the temperature range of $200\,\mathrm{K} < T < 3273.15\,\mathrm{K}$ were calculated

Table 7. Collision Diameters and Well Depths, Using Different Mixing Rules for the Three Binary Interactions between the Components of R404A (44 wt % R125, 4 wt % R134a, and 52 wt % R143a) Ternary Mixture

Mixing rule	Mixture					
	R125–R134a		R125–R143a		R134a–R143a	
	$\sigma/\text{Å}$	$(\varepsilon/k_B)/\text{K}$	$\sigma/\text{Å}$	$(\varepsilon/k_B)/\text{K}$	$\sigma/\text{Å}$	$(\varepsilon/k_B)/\text{K}$
Lorentz–Berthelot	5.168	258.352	4.976	288.486	4.884	316.0098
Halgren-HHG	5.1713	257.816	5.008	285.579	4.8987	315.05
Tang–Toennies	5.1677	258.202	4.975	285.887	4.8839	314.416
Waldman–Hagler	5.1721	256.885	5.0156	272.282	4.9024	307.375
Functional (MADAR-1)	5.1717	257.004	5.0122	273.303	4.9007	308.009
Fit (MADAR-2)	5.1732	255.745	5.0036	274.426	4.8989	307.53

Table 8. Calculated and Literature[33] Viscosities of an Ar–H_2 Mixture[a)]

T/K	η^1_{mix}	η^2_{mix}	η^3_{mix}	η^4_{mix}	η^5_{mix}	η^6_{mix}	$\eta^{33}_{\text{mix (Richenberg)}}$
200	14.8269	14.977	14.9196	14.8995	14.8959	14.8321	14.8007
250	17.9177	18.0848	18.0216	17.9995	17.9954	17.9232	17.8938
273.15	19.2877	19.4656	19.3894	19.3629	19.358	19.2922	19.2718
293.15	20.4097	20.6021	20.5273	20.4966	20.491	20.4149	20.4016
300	20.7914	20.9739	20.906	20.8739	20.8679	20.7219	20.7741
313.15	21.5007	21.6886	21.6177	21.593	21.5884	21.5067	21.4907
333.15	22.583	22.7708	22.6904	22.6624	22.6573	22.5878	22.5732
353.15	23.6361	23.8473	23.7568	23.7254	23.7196	23.6415	23.6368
373.15	24.6331	24.8488	24.7678	24.7326	24.7262	24.6391	24.643
423.15	27.0679	27.2839	27.1915	27.1593	27.1534	27.0734	27.0638
473.15	29.3643	29.6068	29.5176	29.4776	29.4702	29.3711	29.3764
523.15	31.5787	31.8152	31.7141	31.6788	31.6723	31.5848	31.5911
573.15	33.6818	33.9577	33.8425	33.8006	33.7929	33.689	33.6999
623.15	35.6978	35.9708	35.8661	35.8296	35.8229	35.7063	35.7214
673.15	37.6705	37.953	37.8322	37.79	37.7823	37.6777	37.6925
723.15	39.5858	39.9024	39.7706	39.7225	39.7136	39.5941	39.6555
773.15	41.421	41.7391	41.6185	41.5765	41.5653	41.4302	41.4748
873.15	45.0275	45.3805	45.2295	45.1769	45.1672	45.0364	45.1597
973.15	48.4518	48.8347	48.6871	48.6342	48.6224	48.4629	48.6163
1073.15	51.7933	52.2068	52.0298	51.9683	51.957	51.8038	52.0093
1173.15	55.0128	55.4766	55.2917	55.219	55.2056	55.0251	55.2784
1273.15	58.1579	58.6366	58.4399	58.3714	58.3588	58.1724	58.4244
1773.15	73.0636	73.7441	73.4521	73.3506	73.3318	73.0811	73.5361
2273.15	86.7835	87.5952	87.2519	87.1295	87.1068	86.8042	87.2717
2773.15	99.454	100.2969	99.9344	99.8089	99.7857	99.4752	99.8944
3273.15	112.3833	113.1736	112.8394	112.7234	112.7017	112.4138	113.9846

a) The unit of viscosity is (μPa s).

using different mixing rules and tabulated in Table 8. For comparison the viscosities obtained from Richenberg's method[33] have also been included in Table 8. It is worth mentioning that Poling et al.[34] have recommended Richenberg's method as the most consistently accurate method among the other methods cited in their book.

Figure 1 shows the deviations of the calculated viscosities of the Ar–H_2 mixture using six mixing rules, from those computed by the Richenberg method.[33] The absolute average deviations (AAD), were found to be: for Lorentz–Berthelot (0.193%), Halgren-HHG (0.65%), Tang–Toennies (0.31%), Waldman–Hagler (0.18%), Functional (MADAR-1) (0.16%), and Fit (MADAR-2) (0.171%). It is obvious that the Functional (MADAR-1) and Fit (MADAR-2) mixing rules along with Waldman–Hagler give better results while the Halgren-HHG and Tang–Toennies lead to larger AAD's.

The calculated viscosities for methane–ethane and propane–butane binary mixtures are given in Tables 9 and 10, respectively. The results were compared with the viscosities obtained from the NIST Mixture Property Database,[35] which is an interactive program written in standard FORTRAN 77. Figure 2 displays the deviations of calculated viscosities of propane–butane mixture from NIST values.[35]

For the methane–ethane mixture, AAD's of the calculated viscosities from the NIST Mixture Property Database[35] using different mixing rules are given below. Lorentz–Berthelot (0.53%), Halgren-HHG (0.72%), Tang–Toennies (0.82%), Waldman–Hagler (1.72%), Functional (MADAR-1) (0.76%) and Fit (MADAR-2) (0.2%). Here, the Fit (MADAR-2) mixing rule gives the best results. The AAD's are propagated from 0.2% to 1.72%. The considerable differences between AAD's can be attributed to the non similarity of the sizes of mixture

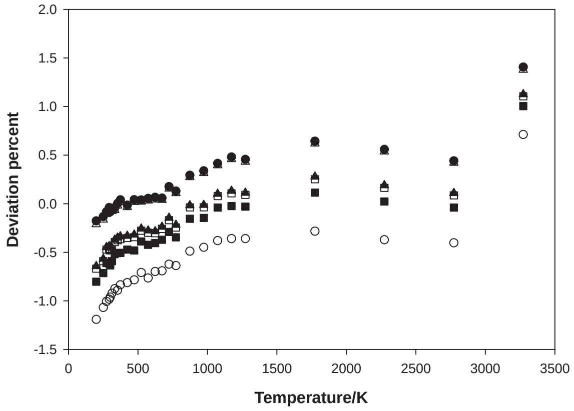

Figure 1. Deviation plot for the calculated viscosity coefficients of Ar–H_2 mixture compared with Richenberg's method[33] using six different mixing rules: Lorentz–Berthelot mixing rule (●), Halgren-HHG[7] (○), Tang–Toennies[8] (■), Waldman–Hagler[3] (□), Functional (MADAR-1)[2] (▲), and Fit (MADAR-2)[2] (△).

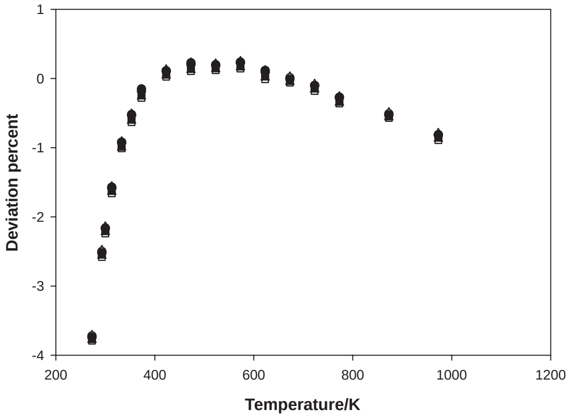

Figure 2. Deviation plot for the calculated viscosity coefficients of a propane–butane mixture compared with the NIST Mixture Property Database[35] using six different mixing rules: Lorentz–Berthelot mixing rule (●), Halgren-HHG[7] (○), Tang–Toennies[8] (■), Waldman–Hagler[3] (□), Functional (MADAR-1)[2] (▲), and Fit (MADAR-2)[2] (△).

Table 9. Calculated and Experimental[35] Viscosities of an Equimolar Methane–Ethane Mixture[a)]

T/K	η^{1}_{mix}	η^{2}_{mix}	η^{3}_{mix}	η^{4}_{mix}	η^{5}_{mix}	η^{6}_{mix}	$\eta^{35}_{\mathrm{mix\ (NIST)}}$
200	7.0037	6.919	7.0401	7.1308	7.0608	7.0041	6.977
250	8.5891	8.4847	8.626	8.727	8.6427	8.5795	8.647
273.15	9.2976	9.1866	9.3492	9.4734	9.3806	9.303	9.387
300	10.1542	10.036	10.2182	10.318	10.22	10.158	10.219
313.15	10.5753	10.445	10.6095	10.7195	10.617	10.548	10.616
333.15	11.1491	11.013	11.1933	11.3197	11.211	11.132	11.207
353.15	11.7286	11.587	11.7841	11.9263	11.813	11.722	11.783
373.15	12.3244	12.177	12.3925	12.4989	12.382	12.317	12.346
423.15	13.7166	13.546	17.7559	13.8924	13.76	13.675	13.698
473.15	15.0659	14.882	15.124	15.2348	15.093	15.024	14.982
523.15	16.3383	16.131	16.364	16.5005	16.345	16.26	16.207
573.15	17.5491	17.329	17.5916	17.7306	17.567	17.485	17.38
623.15	18.7694	18.529	18.7772	18.9033	18.727	18.649	18.508
673.15	19.8658	19.611	19.8819	20.0289	19.841	19.75	19.594
723.15	20.9604	20.693	20.9891	21.1312	20.937	20.854	20.644
773.15	22.0606	21.782	22.0672	22.1952	21.99	21.91	21.66
873.15	24.0574	23.746	24.0637	24.2254	24	23.899	23.603
973.15	26.0326	25.699	26.0247	26.1608	25.92	25.835	25.443

a) The unit of viscosity is (µPa s).

components.

In the case of propane–butane mixture the obtained AAD's are as follows. Lorentz–Berthelot (0.73%), Halgren-HHG (0.65%), Tang–Toennies (0.68%), Waldman–Hagler (0.73%), Functional (MADAR-1) (0.72%), and Fit (MADAR-2) (0.64%). Again it is obvious that the Fit (MADAR-2) mixing rule gives more acceptable results, however, the Halgren-HHG and Tang–Toennies rules also seem to be in the same rank.

Table 11 contains the calculated viscosities of R507A (50 wt % R125 and 50 wt % R143a) binary mixture, together with literature data.[36] The AAD's of calculated viscosities from the experiment[36] using different mixing rules are given below. Lorentz–Berthelot (2.96%), Halgren-HHG (3.3%), Tang–Toennies (2.7%), Waldman–Hagler (2.4%), Functional (MADAR-1) (2.4%), and Fit (MADAR-2) (2.32%). As the AAD's show, the Fit (MADAR-2), stands over other mixing rules. The Waldman–Hagler and Functional (MADAR-1) mixing rules give results as acceptable as the Fit (MADAR-2).

Figure 3 gives the deviations of the calculated viscosity values of binary refrigerant mixture R125–R134a ($X_{\mathrm{R134a}} = 0.249$) at different temperatures, from literature data.[37] The obtained AAD's using different mixing rules are as follows. Lorentz–Berthelot (1.3%), Halgren-HHG (1.31%), Tang–Toennies (1.28%), Waldman–Hagler (1.24%), Functional (MADAR-1) (1.24%), and Fit (MADAR-2) (1.17%). As the results show, using the Fit (MADAR-2) mixing rule, the predicted viscosity values show the best agreement with literature data.[37] It should be mentioned that the Waldman–Hagler and Functional (MADAR-1) take the second rank.

Figure 4 displays deviations of the calculated viscosities of

Table 10. Calculated and Experimental[35] Viscosities of an Equimolar Propane–Butane Mixture[a)]

T/K	η^1_{mix}	η^2_{mix}	η^3_{mix}	η^4_{mix}	η^5_{mix}	η^6_{mix}	$\eta^{35}_{\text{mix (NIST)}}$
273.15	7.4593	7.4576	7.4595	7.4627	7.4618	7.4566	7.1901
293.15	7.905	7.9038	7.906	7.9097	7.9087	7.9026	7.711
300	8.0601	8.0591	8.0614	8.0654	8.0643	8.0579	7.889
313.15	8.3621	8.3615	8.3641	8.3684	8.3672	8.3602	8.2319
333.15	8.8326	8.8329	8.8358	8.8408	8.8394	8.8313	8.752
353.15	9.3184	9.3195	9.3229	9.3286	9.327	9.3177	9.27
373.15	9.8001	9.8023	9.8061	9.8127	9.8108	9.8003	9.785
423.15	11.0456	11.046	11.049	11.055	11.053	11.044	11.058
473.15	12.2741	12.276	12.281	12.289	12.287	12.274	12.302
523.15	13.4885	13.487	13.491	13.498	13.496	13.485	13.514
573.15	14.6574	14.658	14.663	14.671	14.669	14.655	14.692
623.15	15.8181	15.821	15.827	15.837	15.834	15.818	15.836
673.15	16.948	16.945	16.95	16.958	16.955	16.943	16.947
723.15	18.0447	18.043	18.049	18.058	18.055	18.04	18.026
773.15	19.1268	19.127	19.133	19.144	19.141	19.124	19.075
873.15	21.2032	21.198	21.203	21.212	21.21	21.195	21.091
973.15	23.1956	23.193	23.199	23.211	23.207	23.189	23.007

a) The unit of viscosity is (μPa s).

Table 11. Calculated and Experimental[36] Viscosities of R507 (50 wt % R125 and 50 wt % R143a) Binary Mixture[a)]

T/K	η^1_{mix}	η^2_{mix}	η^3_{mix}	η^4_{mix}	η^5_{mix}	η^6_{mix}	$\eta^{36}_{\text{mix (Exp)}}$
299.23	11.89	11.84	11.92	11.95	11.95	11.962	12.239
303.54	12.053	12.004	12.079	12.12	12.11	12.127	12.431
313.81	12.44	12.39	12.47	12.52	12.51	12.527	12.819
322.24	12.77	12.72	12.801	12.85	12.85	12.862	13.178
324.26	12.85	12.8	12.88	12.94	12.93	12.944	13.205
351.45	13.95	13.904	13.99	14.04	14.037	14.054	14.367
383.54	15.16	15.097	15.19	15.22	15.22	15.239	15.689
401.07	15.8	15.734	15.83	15.88	15.87	15.89	16.245

a) The unit of viscosity is (μPa s).

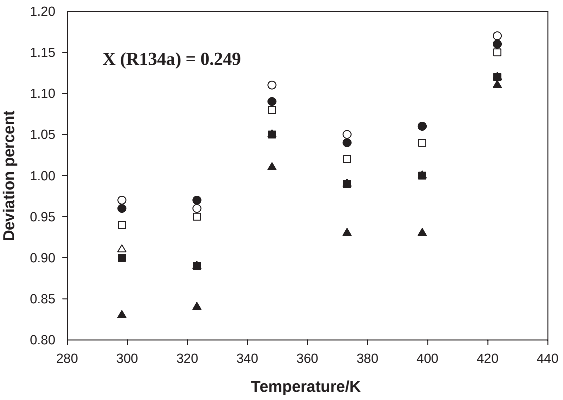

Figure 3. Deviation plot for the calculated viscosity coefficients of a R125–R134a binary mixture ($X_{\text{R134a}} = 0.249$) compared with literature and using six different mixing rules: Lorentz–Berthelot mixing rule (●), Halgren-HHG[7] (○), Tang–Toennies[8] (□), Waldman–Hagler[3] (■), Functional (MADAR-1)[2] (△), and Fit (MADAR-2)[2] (▲).

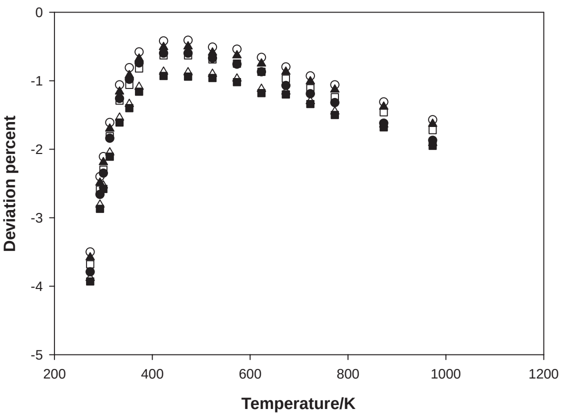

Figure 4. Deviation plot for the calculated viscosity coefficients of an ethane–propane–butane ternary mixture compared with the NIST Mixture Property Database[35] using six different mixing rules: Lorentz–Berthelot mixing rule (●), Halgren-HHG[7] (○), Tang–Toennies[8] (□), Waldman–Hagler[3] (■), Functional (MADAR-1)[2] (△), and Fit (MADAR-2)[2] (▲).

Table 12. Calculated and Experimental[35] Thermal Conductivities of an Equimolar Propane–Butane Mixture[a)]

T/K	$\lambda^{1}_{\mathrm{mix}}$	$\lambda^{2}_{\mathrm{mix}}$	$\lambda^{3}_{\mathrm{mix}}$	$\lambda^{4}_{\mathrm{mix}}$	$\lambda^{5}_{\mathrm{mix}}$	$\lambda^{6}_{\mathrm{mix}}$	$\lambda^{35}_{\mathrm{mix\ (NIST)}}$
273.15	16.01	16.022	16.025	16.031	16.03	16.02	14.4
293.15	18.047	18.063	18.067	18.075	18.073	18.06	16.335
300	18.77	18.786	18.791	18.799	18.796	18.783	17.032
313.15	20.192	20.21	20.216	20.225	20.222	20.207	18.415
333.15	22.447	22.47	22.476	22.488	22.485	22.466	20.627
353.15	24.819	24.846	24.854	24.868	24.864	24.841	22.96
373.15	27.31	27.343	27.353	27.369	27.365	27.338	25.402
423.15	34.003	34.036	34.046	34.064	34.059	34.031	31.91
473.15	41.157	41.206	41.22	41.245	41.238	41.198	38.882
523.15	48.928	48.971	48.984	49.007	49	48.964	46.211
573.15	56.953	57.011	57.028	57.058	57.05	57.001	53.814
623.15	65.49	65.568	65.591	65.631	65.619	65.556	61.624
673.15	74.328	74.391	74.411	74.444	74.434	74.381	69.58

a) The unit of thermal conductivity is ($\mathrm{mW\,m^{-1}\,K^{-1}}$).

ethane–propane–butane ternary mixture from those obtained using the NIST Mixture Property Database.[35] The AAD's are found to be 1.42% for Lorentz–Berthelot, 1.19% for Halgren-HHG, 1.39% for Tang–Toennies, 1.67% for Waldman–Hagler, 1.61% for Functional (MADAR-1), and 1.28% for Fit (MADAR-2). Analysis of AAD's, show that the Halgren-HHG mixing rule stands over the Fit (MADAR-2) mixing rule.

The viscosities of the other ternary mixture, R407C (23 wt % R32, 25 wt % R125, and 52 wt % R134a) were also calculated and compared with literature data.[36] The resulting AAD's of calculated viscosities from literature[36] are: 0.8% for Lorentz–Berthelot, 3.23% for Halgren-HHG, 0.26% for Tang–Toennies, 1.13% for Waldman–Hagler, 1.31% for Functional (MADAR-1), and 1.11% for Fit (MADAR-2). It is observed that the Tang–Toennies mixing rule is the best among other rules and the Halgren-HHG is the worst. Other four mixing rules give almost similar AAD's.

In order to investigate the effect of mixing rules on viscosities of mixtures, having components with significant different sizes, we calculated the viscosities of He–CO_2 and H_2–C_2H_6 binary mixtures, using six mixing rules, and compared the results with those obtained from the Richenberg's method.[33] In the case of He–CO_2 mixture, the AAD's were found to be 0.54% for Lorentz–Berthelot, 2.77% for Halgren-HHG, 2.56% for Tang–Toennies, 2.38% for Waldman–Hagler, 2.62% for Functional (MADAR-1), and 0.59% for Fit (MADAR-2). It is of interest to mention that the Lorentz–Berthelot mixing rule gives the least value of AAD among other mixing rules, however, the Fit (MADAR-2) mixing rule also gives rise to acceptable results.

For the H_2–C_2H_6 mixture, the same study led to the following AADs. Lorentz–Berthelot (0.35%), Halgren-HHG (1.47%), Tang–Toennies (2.52%), Waldman–Hagler (3.32%), Functional (MADAR-1) (3.71%), and Fit (MADAR-2) (1.75%). The results show that again the Lorentz–Berthelot mixing rule stands over other mixing rules when the mixture components have considerably different size and well depth values. The Fit (MADAR-2) mixing rule, which was successful in predicting viscosity values, loses its rank when the mixture components show less size similarity.

It can be concluded that in the case of mixtures with significant difference between their components' size and well depth, 1) the Lorentz–Berthelot mixing rule is superior with respect to other mixing rules, 2) the effect of changing the mixing rule can differentiate between AADs up to 3.5%.

The effect of the aforementioned mixing rules on thermal conductivities was assessed by employing eqs 20–24 and calculating thermal conductivities of two binary and two ternary mixtures by the usage of six different mixing rules.

Table 12 contains the calculated thermal conductivities of an equimolar binary propane–butane mixture, obtained from different mixing rules, in the temperature range of $273.15\,\mathrm{K} < T < 673.15\,\mathrm{K}$. In order to compare, thermal conductivities obtained from the NIST Mixture Property Database[35] have also been included in Table 12. The obtained AADs are: 7.94% for Lorentz–Berthelot, 8.04% for Halgren-HHG, 8.07% for Tang–Toennies, 8.13% for Waldman–Hagler, 8.11% for Functional (MADAR-1), and 8.02% for Fit (MADAR-2). The AADs have near values. Since the same trend was observed for the viscosity of this binary mixture, we can say that the transport properties of propane–butane mixtures are not sensitive to the used mixing rule.

Figure 5 shows the deviations of calculated thermal conductivities of a R507A (50 wt % R125 and 50 wt % R143a) system from literature data.[38] The resulting AADs are: 10.4% for Lorentz–Berthelot, 10% for Halgren-HHG, 10.7% for Tang–Toennies, 11% for Waldman–Hagler, 10.97% for Functional (MADAR-1), and 11.1% for Fit (MADAR-2). The results show that the Halgren-HHG mixing rule leads to more acceptable results for the thermal conductivities of this mixture. The Lorentz–Berthelot takes the second rank and the remaining four mixing rules show almost similar results.

Table 13 lists the calculated thermal conductivities of an equimolar ethane–propane–butane mixture, using different mixing rules, in the temperature range of $273.15\,\mathrm{K} < T < 973.15\,\mathrm{K}$, along with the values obtained from the NIST Mixture Property Database.[35] Figure 6 shows deviations of the calculated thermal conductivities from those obtained using the NIST Mixture Property Database.[35] The AADs for utilized mixing rules are: 11.1% for Lorentz–Berthelot, 10.7% for Halgren-HHG, 10.9% for Tang–Toennies, 11.2% for Waldman–Hagler, 11.2% for Functional (MADAR-1), and

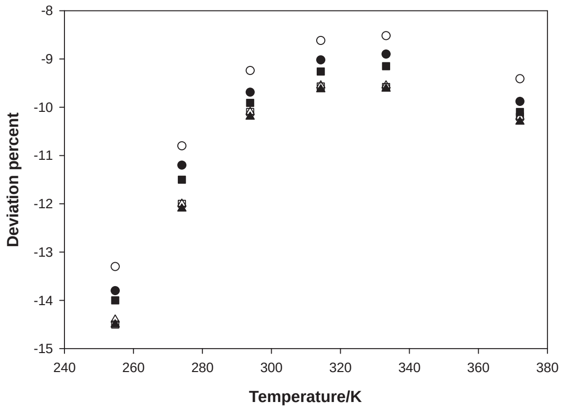

Figure 5. Deviation plot for the calculated thermal conductivities of binary refrigerant mixture, R507A (50 wt% R125 and 50 wt% R143a) compared with the literature data[35] using six different mixing rules: Lorentz–Berthelot (●), Halgren-HHG[7] (○), Tang–Toennies[8] (■), Waldman–Hagler[3] (□), Functional (MADAR-1)[2] (△), and Fit (MADAR-2)[2] (▲).

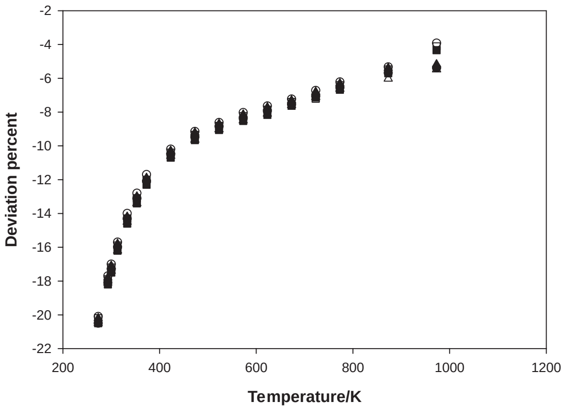

Figure 6. Deviation plot for the calculated thermal conductivities of an ethane–propane–butane ternary mixture compared with the NIST Mixture Property Database[35] using six different mixing rules: Lorentz–Berthelot mixing rule (●), Halgren-HHG[7] (○), Tang–Toennies[8] (□), Waldman–Hagler[3] (■), Functional (MADAR-1)[2] (△), and Fit (MADAR-2)[2] (▲).

Table 13. Calculated and Experimental[35] Thermal Conductivities of an Equimolar Ethane–Propane–Butane Mixture[a)]

T/K	λ^{1}_{mix}	λ^{2}_{mix}	λ^{3}_{mix}	λ^{4}_{mix}	λ^{5}_{mix}	λ^{6}_{mix}	$\lambda^{35}_{\text{mix (NIST)}}$
273.15	18.641	18.577	18.604	18.645	18.641	18.593	15.473
293.15	20.666	20.603	20.637	20.687	20.678	20.619	17.506
300	21.394	21.329	21.367	21.419	21.411	21.348	18.237
313.15	22.835	22.769	22.811	22.87	22.863	22.791	19.684
333.15	25.147	25.082	25.132	25.204	25.194	25.109	21.995
353.15	27.622	27.557	27.619	27.709	27.696	27.592	24.425
373.15	30.221	30.124	30.187	30.277	30.201	30.163	26.962
423.15	37.224	37.124	37.198	37.303	37.287	37.167	33.702
473.15	44.772	44.639	44.721	44.847	44.839	44.669	40.897
523.15	52.731	52.618	52.715	52.832	52.817	52.658	48.442
573.15	60.97	60.774	60.894	61.057	61.308	60.839	56.256
623.15	69.373	69.18	69.32	69.519	69.479	69.242	64.271
673.15	77.896	77.661	77.788	77.956	77.926	77.723	72.428
723.15	86.366	86.092	86.486	86.436	86.41	86.167	80.672
773.15	94.78	94.486	94.658	94.897	94.851	94.567	88.954
873.15	111.46	111.09	111.25	111.48	111.83	111.16	105.471
973.15	128.28	126.53	126.73	127	128.39	128.03	121.722

a) The unit of thermal conductivity is (mW m^{-1} K^{-1}).

10.9% for Fit (MADAR-2). Similar to the case of binary mixtures, the Halgren-HHG leads to the best results among all mixing rules, however all mixing rules give rise to AADs which do not differ from each other by more than 0.5%.

Figure 7, illustrates the deviations of the calculated thermal conductivities of R404A (44 wt% R125, 4 wt% R134a, and 52 wt% R143a) from those given in the literature.[38] AADs for the six aforementioned mixing rules are: 10.8% for Lorentz–Berthelot, 10.4% for Halgren-HHG, 11.1% for Tang–Toennies, 11.4% for Waldman–Hagler, 11.4% for Functional (MADAR-1), and 11.5% for Fit (MADAR-2). Again the Halgren-HHG mixing rule is the best among other mixing rules for this ternary refrigerant mixture. It is noticeable that in spite of the simplicity of the Lorentz–Berthelot mixing rule, it behaves nearly as good as the Halgren-HHG.

Conclusion

This study shows that all the mixing rules are acceptable and the mixture transport properties are affected slightly using different mixing rules, especially when the mixture components do not differ much in size. However, in the case of viscosity, the results are to some extent in favor of the Fit (MADAR-2) mixing rule, but this comes at the expense of two extra adjustable parameters. When the mixture components have considerable difference in their collision diameter and well depth values, the Lorentz–Berthelot mixing rule performs better than other rules in predicting viscosities and the Fit (MADAR-2) rule gains almost the second rank. Other rules do not show an obvious trend so that it is not possible to classify them.

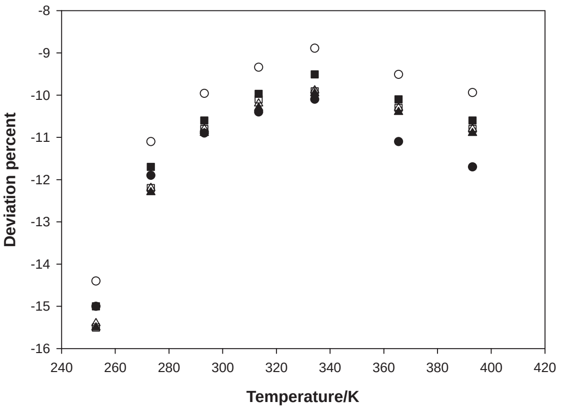

Figure 7. Deviation plot for the calculated thermal conductivities of ternary refrigerant mixture, R404A (44 wt% R125, 4 wt% R134a, and 52 wt% R143a) compared with the literature data[38] using six different mixing rules: Lorentz–Berthelot (●), Halgren-HHG[7] (○), Tang–Toennies[8] (■), Waldman–Hagler[3] (□), Functional (MADAR-1)[2] (△), and Fit (MADAR-2)[2] (▲).

As the difference between the size of components decreases, the effect of mixing rules on the calculated transport properties becomes less important. It is interesting that the Halgren-HHG mixing rule, which is not very successful in predicting viscosities, gives rise to the best results for thermal conductivities. However this rule reduces the errors at most to within ±1%.

The authors express to Research Committees of Shiraz University and Shiraz University of Technology, their sincere thanks due to supporting this project and making computer facilities available.

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