

Thermophysical Properties of Low-Density Pure Alkanes and Their Binary Mixtures Calculated by Means of an ($n-6$) Lennard-Jones Temperature-Dependent Potential¹

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Self-consistent calculations of interaction pVT -virial coefficients $B_{12}(T)$, viscosities $\eta_{\text{mix}}(T)$, and diffusion coefficients $D_{12}(T)$ of binary mixtures of the alkanes C_nH_{2n+2} ($n < 6$) are presented. This study is based on the recently developed model of the ($n-6$) Lennard-Jones temperature-dependent potential (LJTDP) and uses already obtained potential parameters of the pure alkanes as input data. The well-known and simple Lorentz-Berthelot (LB) and the more elaborate Tang-Toennies (TT) mixing rules are applied to the potential parameters of the pure alkanes in order to determine those of the mixtures. The new Hohm-Zarkova-Damyanova (HZD) mixing rule, which is an extension of the TT-mixing rule, is also considered. The HZD takes into account that for the LJTDP model, in general, the repulsive parameter is an independent variable whose value $n \neq 12$. As in a recent examination of binary mixtures of globular molecules, the LB-mixing rule is superior to TT- and HZD-mixing rules when calculating equilibrium properties such as $B_{12}(T)$. For the transport properties $\eta_{\text{mix}}(T)$ and $D_{12}(T)$, the new mixing rule performs slightly better.

KEY WORDS: alkanes; binary diffusion coefficient; binary mixtures; Lennard-Jones temperature-dependent potential; mixing rules; virial coefficient; viscosity.

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1. INTRODUCTION

Thermophysical properties of binary mixtures such as the binary diffusion coefficient $D_{12}(T)$, the viscosity $\eta_{\text{mix}}(T)$, and the second pVT -virial coefficients $B_{\text{mix}}(T)$ are needed for modeling and optimization of technological processes and equipment in a wide range of temperatures. In general, these properties could be measured but the variety of mixtures is not restricted and, apparently, it is not possible to have measured data for each particular case. Therefore, it is desirable to have algorithms which allow for a reliable calculation of the thermophysical properties of mixtures. The theory of gas mixtures [1] presents binary mixture properties as a result of interactions between “equal” (of the same sort A or B) and between “unequal” particles (of two different sorts A and B). Therefore, both sorts of interactions must be known in order to calculate mixture properties.

In this contribution we concentrate on the alkanes C_nH_{2n+2} ($n < 6$), which form the simplest but nevertheless one of the most important homologous series in chemistry. Low-density thermophysical properties of these molecules have been described successfully via the Lennard-Jones temperature-dependent potential, LJTD [2, 3]:

$$U_{AB}(R, T) = \frac{\varepsilon_{AB}(T)}{n_{AB} - 6} \left[6 \left(\frac{R_{mAB}(T)}{R} \right)^{n_{AB}} - n_{AB} \left(\frac{R_{mAB}(T)}{R} \right)^6 \right]. \quad (1)$$

For pure gases we have $A = B$. R is the center-of-mass distance, $R_{mAB}(T)$ is the equilibrium distance, $\varepsilon_{AB}(T)$ is the potential well-depth, and n_{AB} is the repulsive parameter. As already discussed in detail (see, e.g., Ref. 2), the temperature dependence of $R_{mAB}(T)$ and $\varepsilon_{AB}(T)$ is due to the vibrational excitation of the molecules. Therefore, in our model the potential parameters (PP) of, e.g., the noble gases argon, krypton, and xenon would not show any temperature dependence. The repulsive parameter n_{AB} is supposed to be independent of temperature for all particles. The separation between equal molecules is

$$R_{mAA}(T) = R_{mAA}(T = 0 \text{ K}) + \delta_0 f(T), \quad (2)$$

where the product $\delta_0 f(T)$ is the effective enlargement of molecular size caused by the vibrational excitation. δ_0 is a constant (independent of temperature) fit parameter, whereas the function $f(T)$ can be calculated from the vibrational partition function (see Refs. 2 and 4 for details). Assuming that the attractive dispersion-interaction does not depend on the temperature, the potential well-depth for the interaction between equal particles is given by

$$\varepsilon_{AA}(T) = \varepsilon_{AA}(0) [R_{mAA}(0)/R_{mAA}(T)]^6. \quad (3)$$

Within our model and the considered maximum temperature of 1200 K, this is a reasonable assumption. However, one has to bear in mind that the dispersion-interaction energy might show a detectable temperature dependence when dealing with very high temperatures where, e.g., black-body radiation effects become important [5, 6].

The intermolecular interaction potentials $U_{AB}(R, T)$ for unlike interactions between two different alkanes A and B can be obtained by different mixing rules for binary mixtures (see, e.g., Refs. 1, 7, and 8). In our recent studies of binary mixtures between atoms and globular molecules [9], we have applied the Lorentz-Berthelot (LB) as well as the physically more reasonable Tang-Toennies (TT) mixing rules for the potential parameters $R_{mAB}(T)$ and $\varepsilon_{AB}(T)$. The Lorentz-Berthelot mixing rule is given by [1]

$$n_{AB} = (n_{AA} + n_{BB})/2, \quad (4a)$$

$$R_{mAB}(T) = [R_{mAA}(T) + R_{mBB}(T)]/2, \quad (4b)$$

$$\varepsilon_{AB}(T) = \sqrt{\varepsilon_{AA}(T)\varepsilon_{BB}(T)}. \quad (4c)$$

The Tang-Toennies mixing rule can be written in the form [7],

$$(R_{mAB}(T))^{n_{AB}-6} = \frac{\left\{ 0.5[(\varepsilon_{AA}(T))^\varphi (R_{mAA}(T))^\psi + (\varepsilon_{BB}(T))^\varphi (R_{mBB}(T))^\psi] \right\}^{1/\varphi}}{(\varepsilon_{AA}(T)\varepsilon_{BB}(T))^{1/2} (R_{mAA}(T)R_{mBB}(T))^3} \quad (4d)$$

and

$$\varepsilon_{AB}(T) = \left(\varepsilon_{AA}(T)\varepsilon_{BB}(T) \right)^{1/2} \frac{(R_{mAA}(T)R_{mBB}(T))^3}{(R_{mAB}(T))^6} \frac{2\alpha_A\alpha_B (C_6^{AA}C_6^{BB})^{1/2}}{C_6^{AA}\alpha_B^2 + C_6^{BB}\alpha_A^2}, \quad (4e)$$

where α is the dipole-polarizability of the molecule and C_6 is a constant in the leading term $-C_6R^{-6}$ of the dispersion-interaction energy. The original Tang-Toennies mixing rule is derived for the explicit case of a (12-6) Lennard-Jones potential yielding the constants $n_{AB} = 12$, $\varphi = 1/13$, and $\psi = 12/13$ in Eq. (4d) [7].

Many different mixing rules can be found in the literature [8], but generally they are concerned with a (12-6) Lennard-Jones potential. Although rather sophisticated, they all have certain drawbacks in describing the vast amount of thermochemical and thermophysical properties of binary mixtures (see, e.g., Ref. 8). That is why we preferred to use the same approach as in Ref. 7, however, taking into account that in our LJTD model the repulsive parameter n is an independent variable whose

value $n \neq 12$ results from the minimization. The obtained modified Hohm–Zarkova–Damyanova (HZD) mixing rule now uses the parameters $\varphi = 1/(n_{AB} + 1)$ and $\psi = \varphi n_{AB}$ in Eq. (4d).

2. PROCEDURE

The potential parameters of the (n -6) LJTD $U_{AA}(R, T)$ of the pure alkanes were determined by minimizing the sum F of M squared deviations between experimentally obtained (index “exp”) and calculated (index “calc”) thermophysical properties normalized to their individual relative experimental error $a_{i,\text{exp}}$, which is given by the experimentalists. As input data we have used N_η viscosities η , N_B second pVT -virial coefficients B , N_β second acoustic virial coefficients β , and $N_{\rho D}$ binary diffusion coefficients D_{12} , whereas the calculations are performed with the parameterized LJTD, Eq. (1);

$$F = \sum_{i=1}^{N_\eta} \left[\frac{\ln \left(\frac{\eta_{i,\text{calc}}}{\eta_{i,\text{exp}}} \right)}{a_{i,\eta\text{exp}}} \right]^2 + \sum_{i=1}^{N_B} \left[\frac{\ln \left(\frac{B_{i,\text{calc}}}{B_{i,\text{exp}}} \right)}{a_{i,B\text{exp}}} \right]^2 + \sum_{i=1}^{N_\beta} \left[\frac{\ln \left(\frac{\beta_{i,\text{calc}}}{\beta_{i,\text{exp}}} \right)}{a_{i,\beta\text{calc}}} \right]^2 + \sum_{i=1}^{N_{\rho D}} \left[\frac{\ln \left(\frac{(\rho D_{12})_{i,\text{calc}}}{(\rho D_{12})_{i,\text{exp}}} \right)}{(a_{\rho D_{12}})_{i,\text{exp}}} \right]^2. \quad (5)$$

All details concerning the experimental input data $\eta_{i,\text{exp}}$, $B_{i,\text{exp}}$, $\beta_{i,\text{exp}}$, and $\rho D_{i,\text{exp}}$ and their relative uncertainties $a_{i,\text{exp}}$ can be found in Refs. 2 and 3. The obtained LJTD potential parameters at $T = 0$ K and the root-mean-square deviations $\text{RMS} = \sqrt{F/M}$ of the “best” solutions are also given in Refs. 2 and 3 and repeated in Table I. Here, $M = N_\eta + N_B + N_\beta + N_{\rho D}$ is the number of all experimental input data used in our minimization procedure. RMS denotes the root-mean-square deviation of the fit. $\text{RMS} < 1$ means, that the LJTD can reproduce the experimental input data within their stated experimental uncertainty $a_{i,\text{exp}}$; see Ref. 2 for a detailed discussion.

The temperature dependence of $R_{\text{mAA}}(T)$ is given in the form,

$$R_{\text{mAA}}(T) = R_{\text{mAA}}(0) + A_1 \exp(-B_1/T) + A_2 \exp(-B_2/T) \quad (6)$$

where the fit parameters A_1 , A_2 , B_1 , and B_2 can also be found in Table I. Equation (6) can be used for a fast calculation of $R_{\text{mAA}}(T)$ and subsequently $\varepsilon_{AA}(T)$ at any desired temperature T .

Table I. Potential Parameters n , $R_{mAA}(T=0\text{ K})$, $\varepsilon_{AA}(T=0\text{ K})$, δ_0 , Polarizability α , and Dispersion-Interaction Energy Constant C_6 of the Alkanes C_nH_{2n+2} , $n < 6$. (The temperature dependence of $R_{mAA}(T)$ can be calculated via Eq. (6) with the parameters A_1 , B_1 , A_2 , and B_2 . The accuracy of the fit is illustrated by the root-mean-square deviation RMS)

Gas	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂	C(CH ₃) ₄
n	21.63(18)	22.28(5)	24.12(21)	22.72(8)	21.10(4)	22.84(12)	30.48(87)	37.28(29)
$[\varepsilon_{AA}(T=0\text{ K})/k_B]$ (K)	220.78(33)	364.18(35)	478.38(35)	554.42(44)	595.80(31)	682.9(60)	765.2(2.2)	619.02(80)
$R_{mAA}(T=0\text{ K})$ (10^{-10} m)	3.868(2)	4.447(1)	4.930(3)	5.363(4)	5.284(1)	5.537(3)	5.495(2)	5.697(4)
δ_0 (10^{-10} m)	0	0.0241(40)	0.0168(1)	0.0165(1)	0.0195(1)	0.0121(1)	0.0121(1)	0.0070(3)
A_1 (10^{-10} m)	0	0.119997	0.185499	0.264736	0.326082	0.357199	0.313346	0.180731
B_1 (K)	–	605.470	451.278	282.247	339.383	373.522	332.084	443.890
A_2 (10^{-10} m)	0	0.881982	1.09974	1.38971	1.78472	1.61595	1.57872	0.747022
B_2 (K)	–	2149.996	1952.022	1644.370	1758.367	1975.849	1844.566	1963.417
C_6 (au) ^a	129.6	381.8	768.1	1268	1268	1900	1895	1905
α (au) ^a	17.50	29.61	42.09	54.00	54.07	66.0	66.07	66.23
RMS (α_{exp})	0.997	1.487	1.174	0.866	1.393	0.863	0.663	0.958

^aSee Jhanwar and Meath [14] and references therein.

3. RESULTS

3.1. Pure Alkanes

By using the LJTDJ we are able to calculate the thermophysical properties of the pure alkanes mostly within their stated experimental uncertainty a_{exp} , see Table I. This result is independent of their molecular shape and holds for spherically symmetric as well as for small non-spherical alkanes. Moreover, the small dipole moment inherent in some of the alkanes (e.g., propane and n -pentane) does not result in a deterioration of the quality of the results. Therefore, we conclude that our model might be also applicable for other non-spherical and slightly dipolar molecules.

3.2. Binary Mixtures of Alkanes

Given the potential parameters of the pure compounds, the potential parameters of the binary mixtures can be calculated via the combination rule for n_{AB} (see Eq. (4a)) and the two alternative mixing rules for $R_{\text{mAB}}(T)$ and $\varepsilon_{\text{AB}}(T)$ displayed in Eqs. (4b) and (4c) (Lorentz-Berthelot, LB) or Eqs. (4d) and (4e) (original Tang-Toennies, TT, with $n_{\text{AA}} = n_{\text{BB}} = n_{\text{AB}} = 12$, $\varphi = 1/13$, and $\psi = 12/13$, and HZD with $\varphi = 1/(n_{\text{AB}} + 1)$, $\psi = \varphi n_{\text{AB}}$, where the parameter n_{AB} is obtained from Eq. (4a)). Subsequently, the calculation of the mixture and interaction properties is performed following the formulae given by the molecular theory of gases [1], which requires a knowledge of the interaction potential between *equal* ($U_{\text{AA}}(R, T)$ and $U_{\text{BB}}(R, T)$) and *unequal* ($U_{\text{AB}}(R, T)$) particles as a function of the intermolecular distance R and temperature T .

3.3. Comparison with Available Experimental Data

In this section, we compare our results mainly with two sets of experimental data: equilibrium (B_{12}) and transport (η_{mix} and D_{12}) properties. The pVT -interaction virial coefficients $B_{12}^{(\text{Exp})}$ are taken from the recent compilation of Dymond et al. [10], where only the smoothed values are used. A detailed analysis of all experimental values will be the subject of a special review paper [11]. Viscosities η_{mix} and binary diffusion coefficients D_{12} of mixtures are compared mainly to experimental data presented by Abe et al. [12] and augmented by some diffusion data given by Gotoh et al. [13].

As can be seen from Eqs. (4b) to (4e), application of the different mixing rules will result in different parameter sets, $R_{\text{mAB}}(T)$ and $\varepsilon_{\text{AB}}(T)$.

Therefore, within our model the calculated interaction energy given in Eq. (1) differs also for the different mixing rules. Hence, different numerical data in the calculated thermophysical properties can be expected as was already shown in our recent paper, which considers binary mixtures of rare gases with certain quasi-spherically symmetric molecules [9].

In Figs. 1–13 we compare calculated and experimental B_{12} data for several of the possible mixtures between the alkanes C_nH_{2n+2} ($n < 6$). In the figures the difference $\Delta B_{12} = B_{12}^{(LJTDP)} - B_{12}^{(Exp)}$ is displayed as a function of T ; the error bars of the smoothed values are also taken from Ref. 8. In all cases we observe that B_{12} calculated with the Lorentz-Berthelot (LB) mixing rule is closer to the experimental results than calculated with the TT-mixing rule. In five cases all calculated values obtained from the LB-mixing rule are inside the experimental error bars ($CH_4-C_2H_6$, Fig. 1; $C_2H_6-n-C_4H_{10}$, Fig. 8; $C_2H_6-n-C_5H_{12}$, Fig. 9; $C_3H_8-n-C_4H_{10}$, Fig. 10; $C_3H_8-n-C_5H_{12}$, Fig. 11). In all other cases, at least at one temperature, experiment and theory agree within the error bounds. Contrary to this, the TT-mixing rule only gives some results that are in reasonable agreement with experiment. The HZD-mixing rule, however, works only slightly worse compared to the LB rule. Therefore, we conclude that for the alkanes, the LB-mixing rule gives results superior to TT- and HZD-mixing rules when the equilibrium property B_{12} is considered. The same trend for

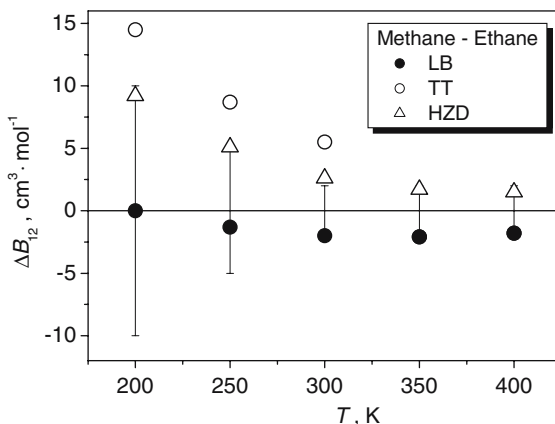


Fig. 1. Deviations $\Delta B_{12} = B_{12}^{(LJTDP)} - B_{12}^{(Exp)}$ of the interaction pVT -virial coefficients for the indicated mixture calculated with Lorentz-Berthelot (filled symbols), Tang-Toennies ($n_{AB} = 12$, $\varphi = 1/13$, and $\psi = 12/13$ in Eq. (4d), open circles) and HZD (open triangles) mixing rules. $B_{12}^{(Exp)}$ is taken from Dymond et al. [10].

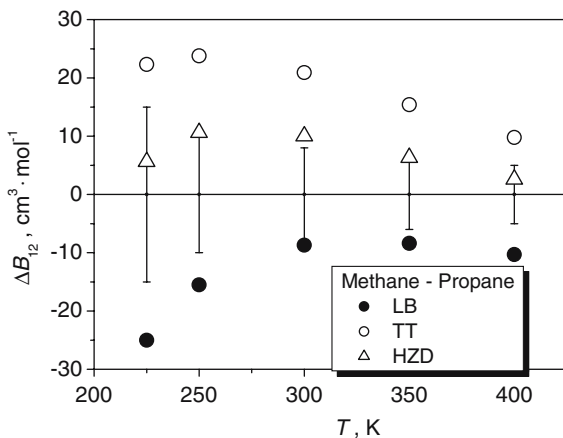


Fig. 2. See Fig. 1.

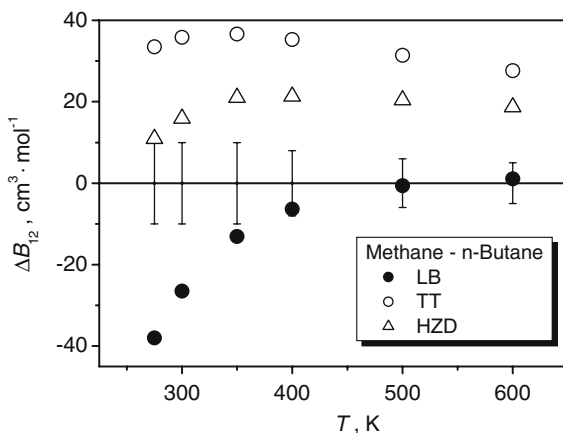


Fig. 3. See Fig. 1.

LB and TT was observed before for binary mixtures between spherically symmetric molecules and noble gases [9].

Abe et al. [12] have measured the viscosities of binary mixtures of different compositions between some of the alkanes considered here. In that work, binary diffusion coefficients are also calculated from the viscosity data by application of the law of corresponding states. The uncertainty of the experimentally obtained η_{mix} is 1%; the uncertainty of D_{12} is estimated by the present authors to be 2%. The deviations $\Delta\eta_{\text{mix}} = 100[\eta_{\text{mix}}^{(\text{Exp})} - \eta_{\text{mix}}^{(\text{LJTDP})}] / \eta_{\text{mix}}^{(\text{LJTDP})}$ and $\Delta D_{12} = 100[D_{12}^{(\text{Exp})} - D_{12}^{(\text{LJTDP})}] / D_{12}^{(\text{LJTDP})}$

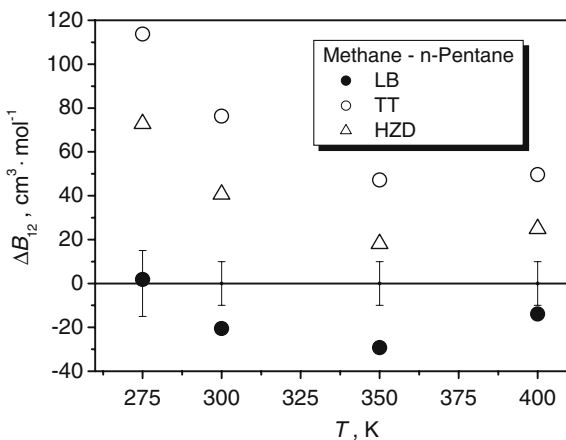


Fig. 4. See Fig. 1.

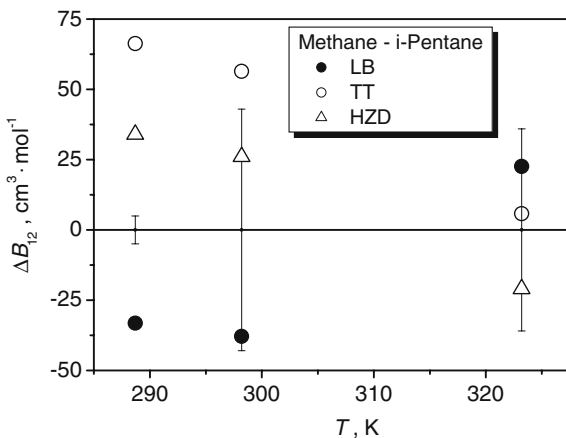


Fig. 5. See Fig. 1.

are shown in Figs. 14–19. In general, we conclude that many of the calculated data lie within the error bars of the experiments. However, application of the TT-mixing rules gives slightly better results for the transport data, η and D . A similar trend was observed before in the case of other binary mixtures [9]. Finally in Figs. 20–22 various absolute values of the binary diffusion coefficient D_{12} are compared. It can be seen that the data of Gotoh et al. [13] are always higher by up to 10% than the corresponding calculated quantities. This is outside the experimental error bar of 3–5% [13]. For the case of the transport data, η_{mix} and D_{12} , the HZD-mixing rule performs nearly exactly like the original TT rule. In

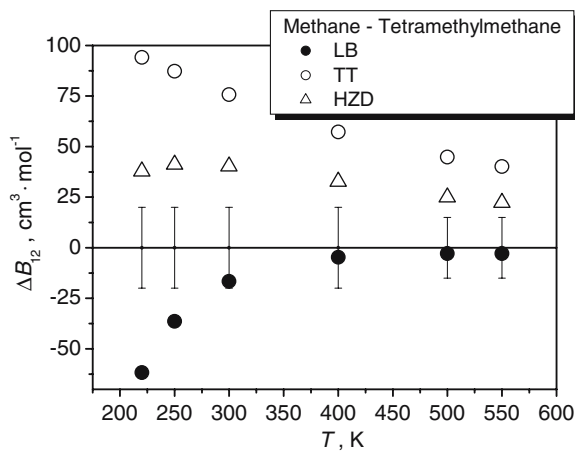


Fig. 6. See Fig. 1.

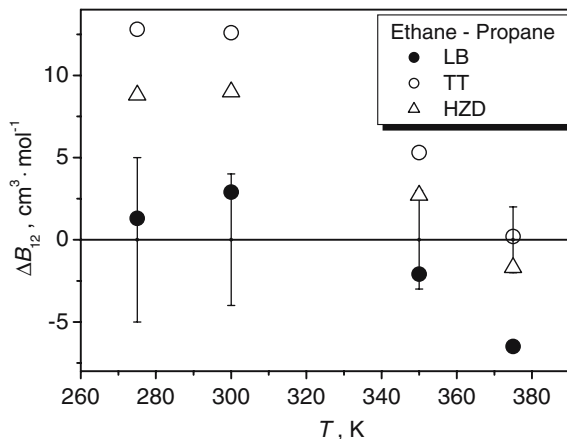


Fig. 7. See Fig. 1.

general, the calculated data do not differ by more than 0.1%. For the sake of clarity, the results from HZD are not displayed in Figs. 14–22.

3.4. Correlation of the Potential Parameters with Other Physically Meaningful Quantities

We have already demonstrated that by using the LJTDPA we are able to calculate some thermophysical properties of the pure alkanes C_nH_{2n+2} ($n < 6$) within their experimental error bars [2, 3]. In this work, we have

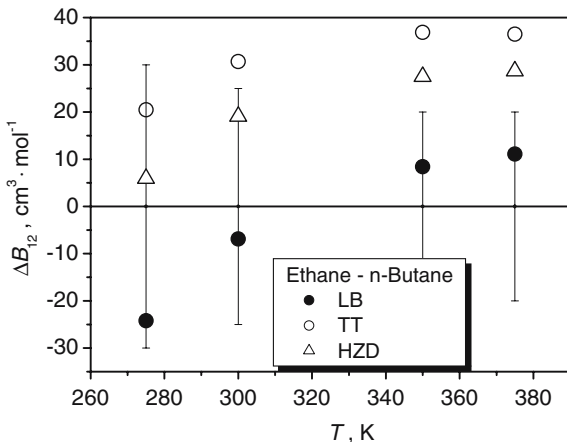


Fig. 8. See Fig. 1.

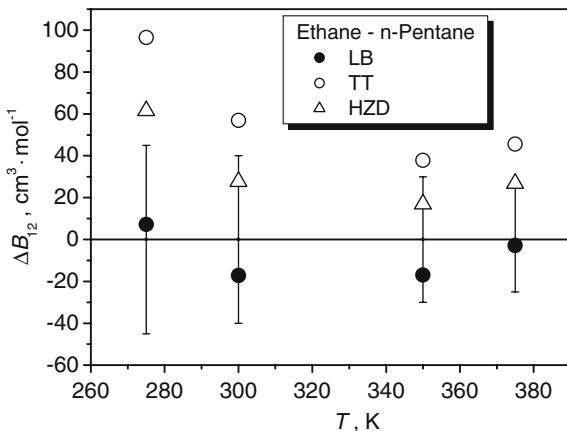


Fig. 9. See Fig. 1.

shown that the application of simple mixing rules on the PP of the pure substances can account for a reasonable accurate calculation of interaction virial coefficients, viscosities, and binary diffusion coefficients. In one of our earlier studies we have revealed [2] that the dispersion-interaction energy constant,

$$C_{6,AB}^* = \frac{n_{AB}\epsilon_{AB}(0)}{n_{AB} - 6} [R_{m AB}(0)]^6 \tag{7}$$

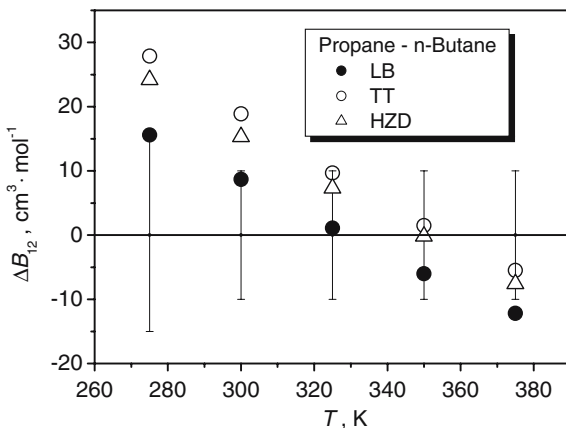


Fig. 10. See Fig. 1.

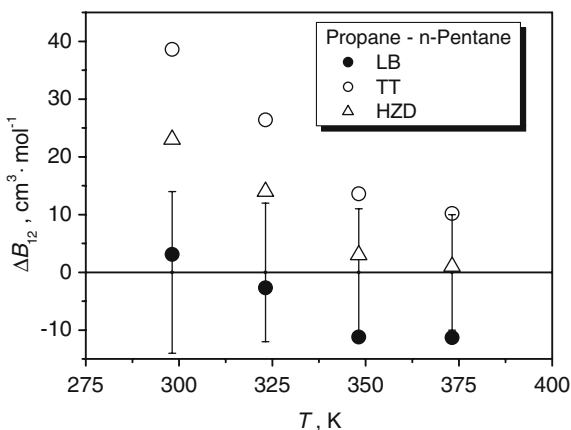


Fig. 11. See Fig. 1.

for the pure alkanes ($A = B$) is linearly related to the exact $C_{6,AA}$ which can be obtained, e.g., from dipole-oscillator strength distributions (DOSDs) [14]. Here we also consider $C_{6,AB}^*$ for the binary mixtures, $A \neq B$, which can be calculated via Eq. (7) by applying the mixing rules Eqs. (4a)–(4e). In Fig. 23 the results for $C_{6,AB}^*$ are compared to $C_{6,AB}$, which again is obtained from DOSDs [14]. Interestingly, we observe the same linear relationship between $C_{6,AB}^*$ and $C_{6,AB}$ for the pure alkanes and their binary mixtures. The quality of this linear relationship is nearly independent of the mixing rule applied. Moreover, no difference between the original TT- and HZD-mixing rules is observed. A least-squares fit shows

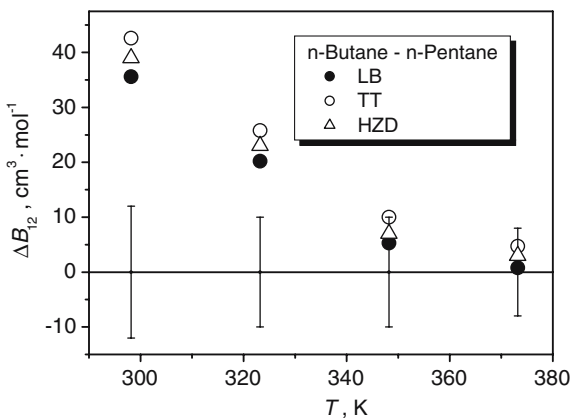


Fig. 12. See Fig. 1.

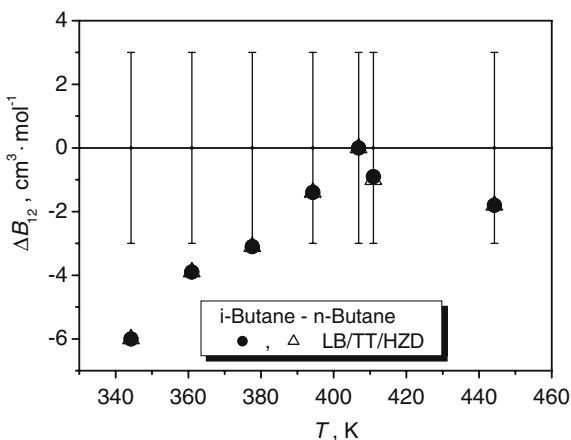


Fig. 13. See Fig. 1.

that $C_{6,AB}^*$ is about twice $C_{6,AB}$. This is expected since the effective $C_{6,AB}^*$ also contains contributions from higher-order dispersion-interaction energies. The linear relationship might give a route for calculating $C_{6,AB}^*$ values from known $C_{6,AB}$, because the latter ones are available from spectroscopic data of the pure entities.

A second linear relation has been observed between $R_{m AA}(0)$ and the cube root of the molecular volume $V_{m,A}^{1/3}$, as defined by the 0.001 au envelope of the electronic density [2]. We also additionally consider in this case the properties of binary mixtures. Here we define the length

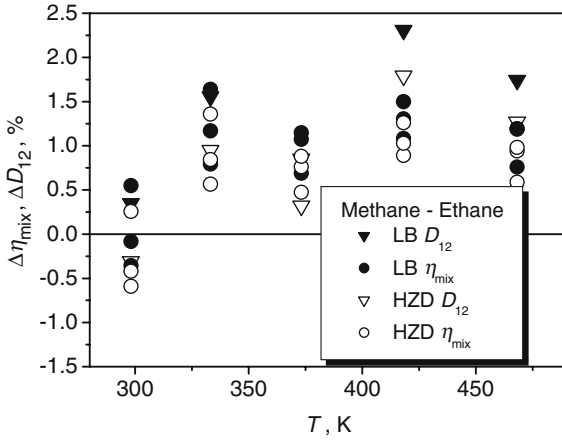


Fig. 14. Relative deviations of viscosity $\Delta\eta_{\text{mix}} = 100[\eta_{\text{mix}}^{(\text{Exp})} - \eta_{\text{mix}}^{(\text{LJTDP})}]/\eta_{\text{mix}}^{(\text{LJTDP})}$ and diffusion coefficient $\Delta D_{12} = 100[D_{12}^{(\text{Exp})} - D_{12}^{(\text{LJTDP})}]/D_{12}^{(\text{LJTDP})}$ for the indicated mixture calculated with Lorentz-Berthelot (filled symbols) and HZD (open symbols) mixing rules. Results for $\eta_{\text{mix}}^{(\text{LJTDP})}$ and $D_{12}^{(\text{LJTDP})}$ calculated with the TT-mixing rules differ by no more than 0.2% from the HZD data and are not displayed. $\eta_{\text{mix}}^{(\text{Exp})}$ and $D_{12}^{(\text{Exp})}$ are taken from Abe et al. [12] with $\eta_{\text{mix}}^{(\text{Exp})}$ given at different compositions.

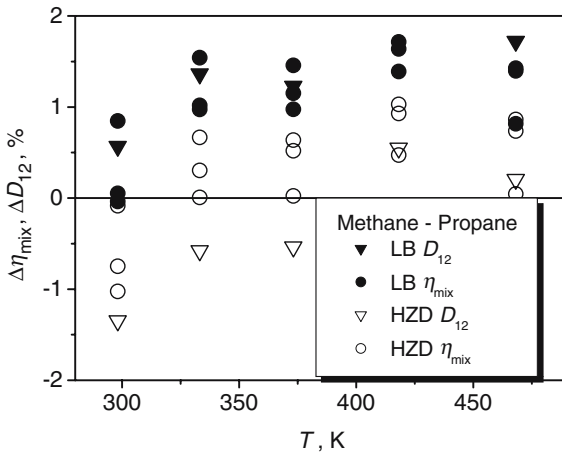


Fig. 15. See Fig. 14.

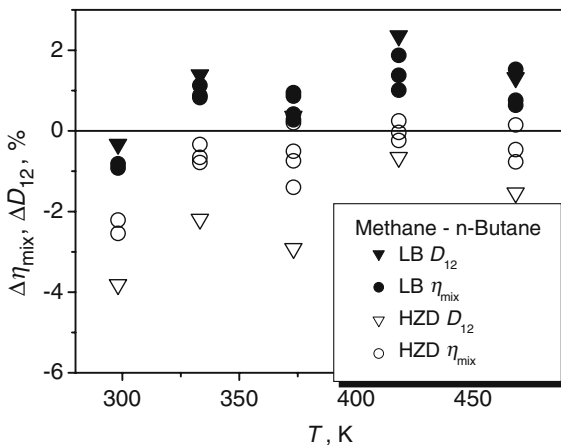


Fig. 16. See Fig. 14.

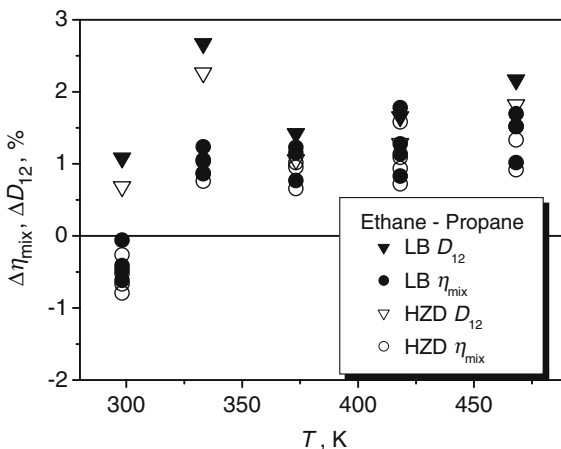


Fig. 17. See Fig. 14.

parameter for a binary mixture via

$$V_{m,AB}^{1/3} = \left(\frac{V_{m,A} + V_{m,B}}{2} \right)^{1/3} \quad (8)$$

In Fig. 24 $R_{m,AB}(0)$ is plotted against $V_{m,AB}^{1/3}$. As can be seen, the same linear relationship exists between $R_{m,AB}(0)$ and $V_{m,AB}^{1/3}$ for pure substances and binary mixtures. In this case $R_{m,AB}(0)$ calculated from the TT-mixing

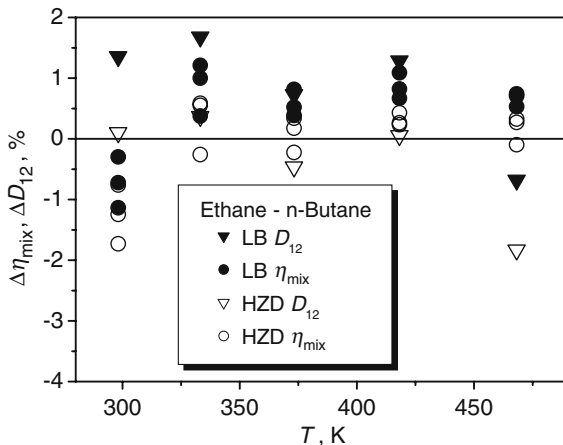


Fig. 18. See Fig. 14.

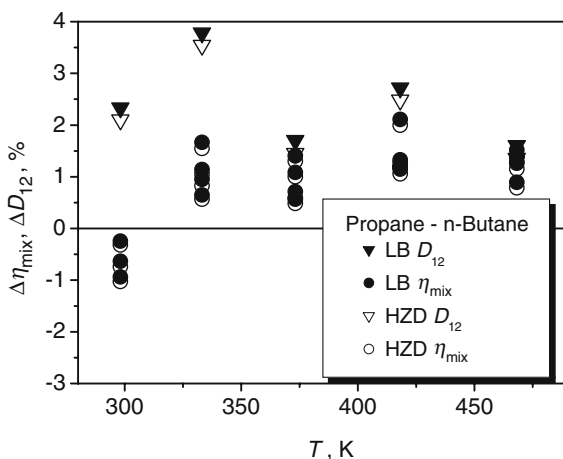


Fig. 19. See Fig. 14.

rule gives a slightly better correlation with $V_{\text{m,AB}}^{1/3}$ compared to the LB-mixing rule. Again, the differences between TT- and HZD-mixing rules are negligible.

Another different length parameter of a molecule can be obtained from its critical volume. In Fig. 25 we have plotted $R_{\text{m AB}}(0)$ against the cube root of the critical volume $V_{\text{C,AB}}^{1/3}$, again for both pure substances ($A=B$) and binary mixtures ($A \neq B$). In the latter case $V_{\text{C,AB}}^{1/3}$ is calculated

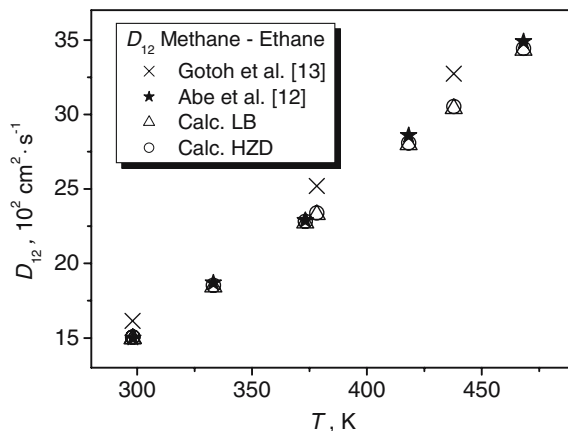


Fig. 20. Comparison of experimental [12, 13] and calculated values of D_{12} for $\text{CH}_4\text{-C}_2\text{H}_6$.

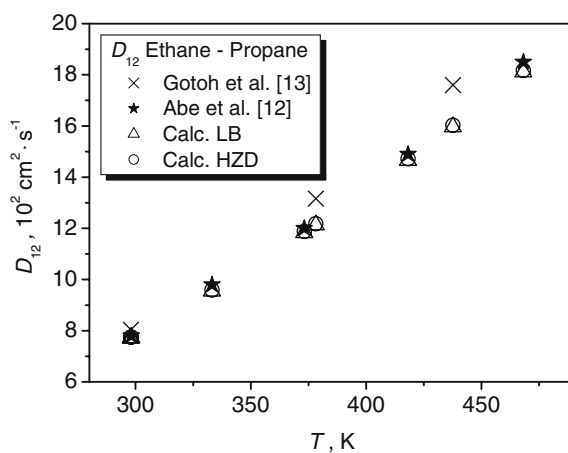


Fig. 21. Comparison of experimental [12, 13] and calculated values of D_{12} for $\text{C}_2\text{H}_6\text{-C}_3\text{H}_8$.

from the pure substance data via [15]

$$V_{C,AB}^{1/3} = \frac{1}{2} \left(V_{C,A}^{1/3} + V_{C,B}^{1/3} \right). \quad (9)$$

Again a linear relationship is found. In this case our results obtained from the Lorentz-Berthelot mixing rule give a slightly better linear correlation

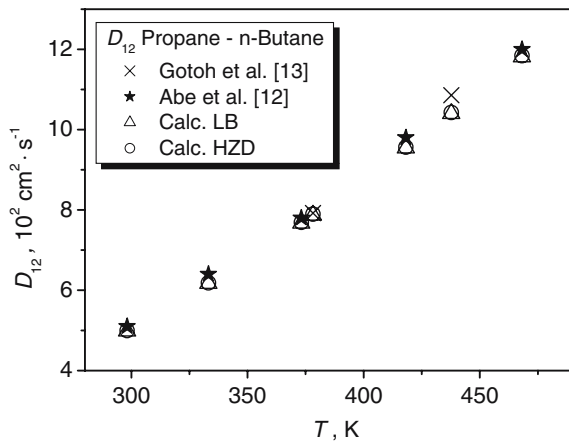


Fig. 22. Comparison of experimental [12, 13] and calculated values of D_{12} for C_3H_8 - n - C_4H_{10} .

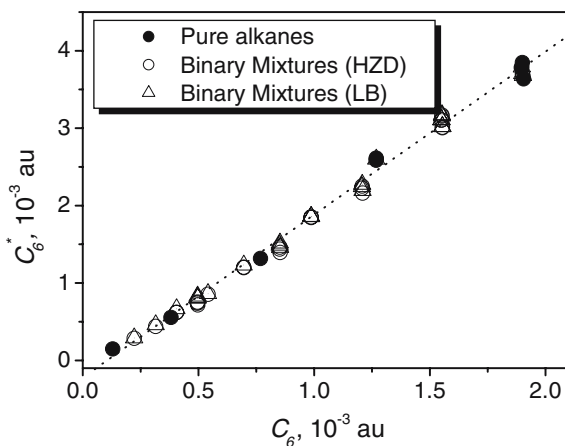


Fig. 23. Dispersion-interaction energy constant $C_{6,AB}^*$ calculated in this work against $C_{6,AB}$ obtained from dipole-oscillator strength distributions (DOSDs) [14]. The dashed line is a linear least-squares fit using all pure and mixture data, which are obtained from the LB-mixing rule. For the sake of clarity, the results from the TT-mixing rule are not displayed; see text.

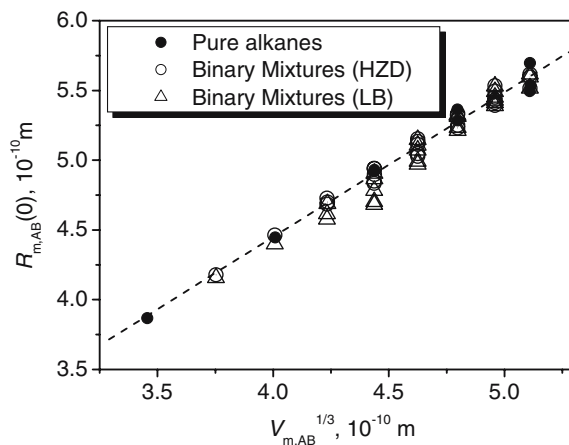


Fig. 24. $R_{m,AB}(0)$ as a function of the cube-root $V_{m,AB}^{1/3}$ of the molecular volume. The dashed line is a linear least-squares fit using all pure and mixture data, which are obtained from the HZA-mixing rule. For the sake of clarity, the results from the TT-mixing rule are not displayed; see text.

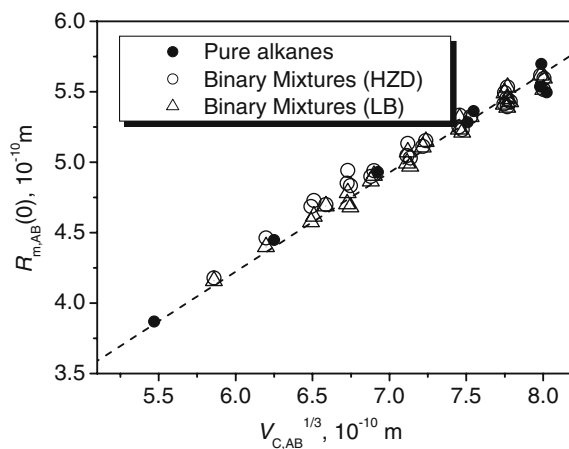


Fig. 25. $R_{m,AB}(0)$ as a function of the cube-root $V_{C,AB}^{1/3}$ of the critical volume. The dashed line is a linear least-squares fit using all pure and mixture data, which are obtained from the LB-mixing rule. For the sake of clarity, the results from the TT-mixing rule are not displayed; see text.

compared to TT and HZD. It is noteworthy that in this plot only experimentally accessible quantities are related to each other.

4. CONCLUSION

We have applied the Lorentz-Berthelot (LB), Tang-Toennies (TT), and a modified version of the Tang-Toennies mixing rule, called the Hohm–Zarkova–Damyanova (HZD) mixing rule to calculate the potential parameters of the LJTD model of binary mixtures. We have demonstrated that these mixing rules are able to account for the calculation of viscosities η , pVT second virial coefficients B , and binary diffusion coefficients D_{12} of low-density binary mixtures nearly within their experimental error bounds. Although the original Tang-Toennies (TT) mixing rules have a deeper physical background, they are not superior to the Lorentz-Berthelot (LB) mixing rules when calculating thermophysical properties within our LJTD model. As has already been observed in one of our recent studies, the LB-mixing rule works much better compared to the original TT-mixing rule for the case of the interaction virial coefficient B_{12} and only slightly worse for viscosities η_{mix} and binary diffusion coefficients D_{12} . However, we observe a much better performance of the HZD compared to the TT-mixing rules when dealing with B_{12} . For the case of the transport properties the difference between TT- and HZD-mixing rules are negligible. This trend should become more pronounced in a further study when thermophysical property reference data for low-density binary mixtures of the alkanes are available.

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