Binary diffusion coefficients of low-density mixtures of alkanes

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Abstract. The aim of this study is to present a reliable procedure for the calculation of the temperature dependencies of binary diffusion coefficients $D_{AB}$ of low-density mixtures of small alkanes $C_mH_{2m+2}$ ($m < 6$) by means of the $(n_{AB}-6)$ Lennard Jones temperature dependent potential (LJTDP) in the temperature range 200 - 1200 K and pressures $p \leq 0.10$MPa. The parameters of the potential of interaction of unlike particles – potential well depth $\varepsilon_{AB}(T)$ and equilibrium distance $R_{mAB}(T)$ are obtained from corresponding pure alkanes potential parameters using the Hohm-Zarkova-Damyanova (HZD) mixing rule. A good agreement between the calculated and experimental values is obtained for those systems for which direct measurements and recalculations from mixture viscosity data are available.

1. Introduction
The binary diffusion coefficients data $D_{AB}$ of the alkanes, which are constituents of the natural gas, are required in modeling and optimization of the technological processes and equipment in a wide temperature range.

In 1972 Marrero and Mason published a paper [1] devoted to the gas diffusion where they considered existing experimental techniques and gave a detailed survey of the experimental results and theory of binary and multicomponent gas mixtures of some non-polar and polar molecules. Some of the diffusion coefficient data available in the literature are directly measured, whereas some are recalculated from the viscosity $\eta_{AB}$. The second method is widely used to calculate $D_{AB}$ of heavy particles. It compensates for the scarcity of experimentally measured diffusion coefficients and its accuracy is comparable with that of the most precisely measured diffusion data. Usually such data are considered as “experimental” ones.

2. Theoretical background
The pair-wise interactions between two molecules of the type $C_mH_{2m+2}$ ($m \leq 5$) were investigated via the isotropic $(n_{AB}-6)$ Lennard-Jones temperature dependent potential, LJTDP, [2].

$$U_{AB}(R,T) = \frac{\varepsilon_{AB}^{(eff)}(T)}{n_{AB} - 6} \left\{ 6 \left( \frac{R_{mAB}^{(eff)}(T)}{n_{AB}} \right)^{n_{AB}} - n_{AB} \left( \frac{R_{mAB}^{(eff)}(T)}{R} \right)^6 \right\},$$

(1)
where \( R_{\text{mAB}}^{(\text{eff})}(T) \) and \( \varepsilon_{\text{AB}}^{(\text{eff})}(T) \) are the effective equilibrium distance and potential well-depth, respectively; \( n_{\text{AB}} \) is the repulsive parameter, which we assume not to depend on the temperature, and \( R \) is the center-of-mass distance. The unlike interaction parameters \( R_{\text{mAB}}^{(\text{eff})}(T) \), \( \varepsilon_{\text{AB}}^{(\text{eff})}(T) \), and \( n_{\text{AB}} \) are obtained from those of the pure substances via the Hohm-Zarkova-Damyanova (HZD) mixing rules [2].

\[
\left( R_{\text{mAB}}^{(\text{eff})}(T) \right)^{\text{AB}} = \left\{ \frac{0.5 \left[ \varepsilon_{\text{AA}}^{(\text{eff})}(T) R_{\text{mAB}}^{(\text{eff})}(T) + \varepsilon_{\text{BB}}^{(\text{eff})}(T) R_{\text{mAB}}^{(\text{eff})}(T) \right]}{\varepsilon_{\text{AA}}^{(\text{eff})}(T) R_{\text{mBB}}^{(\text{eff})}(T)} \right\}^{1/2},
\]

(2)

\[
\varepsilon_{\text{AB}}^{(\text{eff})}(T) = \left( \varepsilon_{\text{AA}}^{(\text{eff})}(T) \varepsilon_{\text{BB}}^{(\text{eff})}(T) \right)^{1/2} \left( \frac{R_{\text{mAB}}^{(\text{eff})}(T) R_{\text{mBB}}^{(\text{eff})}(T)}{R_{\text{mAA}}^{(\text{eff})}(T)} \right)^{2/3} 2\alpha_A \alpha_B \left( C_6^{\text{AA}} C_6^{\text{BB}} \right)^{1/3},
\]

(3)

with

\[
\varphi = \frac{1}{1 + n_{\text{AB}}}, \quad \psi = \frac{n_{\text{AA}} + n_{\text{BB}}}{2}.
\]

(4)

where \( \alpha_A \) and \( \alpha_B \) are the dipole-polarizabilities, and \( C_6^{\text{AA}} \) and \( C_6^{\text{BB}} \) are the dispersion-interaction energy constants of molecules A and B, respectively.

Subsequently these parameters allow for a calculation of the interaction viscosity \( \eta_{\text{AB}} \) within the kinetic theory of gases [3].

\[
\eta_{\text{AB}} = \frac{5}{16\pi N_A \sigma_{\text{AB}}^2(T)} \Omega_{\text{AB}}^{(2,2)}(T^*) \left( \frac{2\pi k_B T N_A M_B}{M_A + M_B} \right)^{1/2},
\]

(5)

where \( M_A \) and \( M_B \) are the molar masses of the two molecules A and B, \( T^* = k_B T / \varepsilon_{\text{AB}}^{(\text{eff})}(T) \) is the reduced temperature, \( \sigma_{\text{AB}}(T) = \frac{R_{\text{mAB}}^{(\text{eff})}(T)}{(n_{\text{AB}} / 6) \left( \sigma_{\text{AB}}^{(6)} \right)^{6/2}} \), \( k_B \) and \( N_A \) being Boltzmann’s and Avogadro’s constants, respectively, and \( \Omega_{\text{AB}}^{(2,2)}(T^*) \) is the reduced viscosity collision integral.

In first approximation

\[
D_{\text{AB}} = \frac{3}{5} \frac{k_B N_A T M_A + M_B}{M_A M_B} A_{\text{AB}}^{*} \eta_{\text{AB}}.
\]

(6)

Here, \( p \) is a pressure, \( A_{\text{AB}}^{*} = \Omega_{\text{AB}}^{(2,2)^*} / \Omega_{\text{AB}}^{(4,1)^*} \) is a ratio of the reduced collision integrals \( \Omega_{\text{AB}}^{(4,1)^*}(T^*) \) and \( \Omega_{\text{AB}}^{(2,2)^*}(T^*) \), where \( \Omega_{\text{AB}}^{(4,1)^*}(T^*) \) is the reduced diffusion collision integral.

3. Comparison with available experimental data and calculated results of other authors

The potential parameters for the pure alkanes were obtained earlier [4].

Our literature survey revealed that there are no directly measured diffusion coefficients for binary mixtures between alkanes containing either \( n\text{-C}_5\text{H}_{12} \) or \( i\text{-C}_5\text{H}_{12} \). The available experimental data points for \( D_{\text{AB}} \) are presented in table 1. The direct measurements are published in [6, 8, 9, 11], whereas the rest of the data [7,10,12] (marked in the table 1 by *) are re-calculated from measured viscosities via equation (6).

The relative deviations between the calculated and measured diffusion coefficients \( D_{\text{AB}} \) of the mixture \( \text{CH}_4\text{-C}_2\text{H}_6 \) are shown in figure 1 as a typical example. As it is seen, the \( D_{\text{AB}} \) data measured by Trautz and Müller [6] deviate the most from our calculations. The same holds true also for the mixtures \( \text{CH}_4 \text{- C}_3\text{H}_8 \) and \( \text{C}_2\text{H}_6 \text{- C}_3\text{H}_8 \). The experimental data of Arora et al. [11] are shown as a curve.
The authors have measured binary diffusion coefficients over the temperature range 275-323 K at constant mole fraction and then fitted them to polynomials. Direct experimental values of the binary diffusion coefficient at 298 K for the systems CH₄-C₂H₆ and C₂H₆-C₃H₈ are given by Gover [8]. The deviations of his data from ours are less than 2%. Binary diffusion coefficients of 24 mixtures of alkanes were determined at atmospheric pressure and between 298 K and 438 K by Gotoh et al. [9]. These authors also predict diffusion coefficients in the same temperature range. The deviations of their calculated results from the measured values are in the frame of 0.1-13.2%.

The data of Abe et al. [10], Kestin and Yata [12], and Weissmann [7] are re-calculated from experimental viscosities. Their calculations are in a very good agreement with our results. At the same time the results of Abe et al. [13] for the mixture n-C₄H₁₀ - i-C₄H₁₀ look rather suspicious. The deviations of $D_{AB}$ reach 90%, while the $\eta_{AB}$ and $\eta_{mix}$ deviations do not exceed $\pm1.5\%$ and $\pm1.0\%$, respectively. An explanation of this discrepancy is yet to be found.
Figure 1. Relative deviations between calculated and measured diffusion coefficients $D_{AB}$ of the mixture CH$_4$-C$_2$H$_6$.

Conclusion

The $(n_{AB}-6)$ LJTDP is used to obtain diffusion coefficients in a large temperature range (200 - 1200K) for 28 binary mixtures of eight alkanes C$_m$H$_{2m+2}$ ($m<6$). The $(n_{AB}-6)$ LJTDP parameters of the mixtures were calculated by means of the HZD mixing rule. A good agreement is obtained for 20 binary mixtures. There is strong need for further experimental studies on the thermophysical properties of binary mixtures which can help to check and improve our approach of the application of the LJTDP to mixtures.

References

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