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Correlations

Effective (*n*-6) Lennard-Jones Potentials with Temperature-Dependent Parameters Introduced for Accurate Calculation of Equilibrium and Transport Properties of Ethene, Propene, Butene, and Cyclopropane[†]

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The alkenes and cycloalkanes C_mH_{2m} ($m = 1$ to 4) are important reactants, intermediates, and end products in the chemical industry. Some of them are also widely used in the polymer industry. This paper presents tables with recommended thermophysical data in the temperature range (200 to 1000) K and pressures $\leq$ 0.1 MPa of ethene, propene, cyclopropane, 1-butene, *cis*-2-butene, *trans*-2-butene, and iso-butene. Second *pVT* virial coefficients B, viscosities η, and diffusion coefficients D are calculated by means of a (n-6) Lennard-Jones temperature-dependent potential. The potential parameters, equilibrium distance $R_m(T)$, and potential well-depth $\varepsilon(T)$ are defined as functions of the temperature T by solving an ill-posed problem of minimization of the squared deviations between measured and calculated B, η, and D, normalized to their experimental error. Tables with potential parameters as well as algorithms for calculation of the potential-dependent properties are given in this paper.

Introduction

The lower alkenes C_mH_{2m} are important reactants, intermediates, or end products in the chemical industry. Especially ethene (ethylene, C_2H_4), propene (propylene, C_3H_6), 1-butene (1-butylene), *cis*-2-butene (*cis*-2-butylene), and iso-butene (iso-butylene, all butenes C_4H_8) are important monomers in the polymer industry.[1] In many cases, the polymerization is carried out in the gas phase using not only the pure monomers but also binary and ternary mixtures of some alkenes.[1−14] It is clear that for a better understanding and modeling of the underlying physical and chemical processes the thermophysical and thermochemical properties of the alkenes must be known. To this end, many experimental and theoretical studies on the thermophysical properties and the equation of state of the lower alkenes have been carried out.[15−21] These studies are augmented by detailed analyses of the underlying intermolecular interaction potentials.[22−29] Knowing the intermolecular interaction energy $U(R,\omega)$ as a function of distance R and mutual orientation ω, some of the thermophysical properties of bulk matter can be calculated.[30] In this work, we apply our model of the (n-6) Lennard-Jones temperature-dependent potential, (n-6) LJTDP, to calculate and predict the second *pVT* virial coefficient B, the viscosity η, and the diffusion coefficient D of the low density alkenes C_mH_{2m}, $m < 5$. The LJTDP has been successfully applied before to a number of pure gases like the alkanes[31,32] and perfluoroalkanes.[33] We have shown that it performs also very well in the prediction of B, η, and D of binary mixtures of alkanes and other gases.[34,35] To give a comprehensive overview on the molecules with sum formula C_mH_{2m}, we not only consider the alkenes but also try to include the two cyclic compounds cyclopropane (C_3H_6) and cyclobutane (C_4H_8) in our studies. These two molecules are also of some importance in industry[36−38] and basic research.[39]

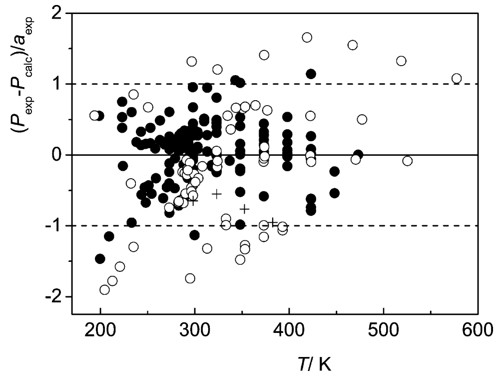

Figure 1. Deviations $P_{exp} - P_{calc}$ between experimental and calculated properties $P = B$, η, or ρD, for ethene, C_2H_4, normalized to their individual experimental uncertainties a_{exp}: ●, second *pVT* virial coefficients B; ○, viscosities η; +, diffusion coefficients ρD.

Theoretical Section

In this section, we follow closely our procedures which have been presented in detail, e.g., by Hohm et al.[33] For the sake of clarity, the basic ideas are repeated in the following section.

Potential Model. The (n-6) LJTDP is an effective spherical potential with explicitly temperature-dependent potential parameters

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Table 1. Table of Experimental Input Data

molecule	reference	property	no., N_i, of input data	ΔT/K	relative experimental error, a_exptl/%
ethene	Roper[43] (1940)	B	5	198 to 343	2 to 5
	Michels and Geldermans[44] (1942)	B	13	273 to 398	1 to 3
	Ashton and Halberstadt[45] (1958)	B	3	300 to 337	2.8 to 3.7
	Lee and Edmister[46] (1970)	B	2	348.2	1.5
	Göpel and Dorfmüller[47] (1972)	B	5	199 to 343	0.1 to 0.3
	Pompe and Spurling[48] (1974)	B	10	273 to 423	1.6 to 5
	Trappeniers et al.[49] (1975)	B	13	273 to 423	1.8 to 2
	Douslin and Harrison[50] (1976)	B	21	238 to 448	1
	Lee[51] (1976)	B	10	243 to 292	0.6 to 0.9
	Waxman and Davis[52] (1979)	B	8	273 to 448	1 to 1.5
	Prasad and Viswanath[53] (1980)	B	6	298 to 423	2 to 3
	Levelt Sengers and Hastings[54] (1981)	B	6	223 to 273	1 to 1.5
	Findeisen and Raetzsch[55] (1981)	B	5	298 to 398	2.5 to 4
	Ohgaki et al.[56] (1981)	B	2	298	4
	Ohgaki et al.[57] (1982)	B	2	398	2
	Lehmann et al.[58] (1983)	B	3	323 to 373	11 to 12
	Ohgaki et al.[59] (1984)	B	2	423 to 473	1.5 to 4
	Mollerup[60] (1985)	B	1	310	1
	Häusler and Kerl[61] (1988)	B	4	282 to 318	5
	Achtermann et al.[62] (1990)	B	8	283 to 373	1.5 to 2
	Lopatinskii et al.[63] (1991)	B	2	293	2.5
	Bell et al.[64] (1992)	B	3	290 to 310	4
	McElroy and Fang[65] (1993)	B	6	283 to 333	6
	Gainar and Anitescu[66] (1994)	B	2	298	1 to 8
	Duarte et al.[67] (2002)	B	1	273	1
	Titani[68] (1930)	η	10	293 to 393	3
	Trautz and Stauf[69] (1929)	η	13	193 to 525	3
	Trautz and Melster[70] (1930)	η	3	292 to 374	3
	Trautz and Heberling[71] (1931)	η	6	291 to 423	3
	Van Cleeve and Maas[72] (1935)	η	11	192 to 296	3
	Lambert et al.[73] (1955)	η	8	308 to 364	2
	Kestin et al.[74] (1971)	η	2	296 to 303	3
	Iwasaki and Takahashi[75] (1975)	η	4	282 to 298	1
	Timrot et al.[76] (1975)	η	7	296 to 577	1
	Kestin et al.[77] (1977)	η	5	300 to 477	1.5 to 3
	Dunlop[78] (1994)	η	1	298.15	1
	Mueller and Cahill[79] (1964)	ρD	3	298 to 348.15	10
	Takahashi[80] (1977)	ρD	3	298 to 382.5	10
propene	Roper[43] (1940)	B	8	223 to 308	1.9 to 2
	Michels et al.[81] (1953)	B	7	298 to 423	1.9 to 2.2
	McGlashan and Wormald[82] (1964)	B	12	304 to 414	2.8 to 3.7
	Pompe and Spurling[48] (1974)	B	38	278 to 573	1.5
	Bier et al.[83] (1974)	B	5	323 to 398	0.1 to 0.3
	Warowny and Stecki[84] (1978)	B	3	393 to 423	1.6 to 5
	Warowny et al.[85] (1978)	B	9	380 to 423	1.8 to 2
	Ohgaki et al.[56] (1981)	B	2	298	1
	Ohgaki et al.[57] (1982)	B	2	398	0.6 to 0.9
	Ohgaki et al.[59] (1984)	B	2	423 to 473	1 to 1.5
	Mollerup[60] (1985)	B	5	270 to 345	2 to 3
	Lopatinskii et al.[63] (1991)	B	1	293	1 to 1.5
	Gainar and Anitescu[66] (1994)	B	2	298	1 to 10
	Titani[68] (1930)	η	7	293 to 393	3
	Trautz and Husseini[86] (1934)	η	10	289 to 523	3
	Van Cleeve and Maas[72] (1935)	η	13	192 to 296	3
	Adzumi[87] (1937)	η	8	303 to 373	3
	Lambert et al.[73] (1955)	η	8	308 to 363	2
cyclopropane	Ruehrwein and Powell[88] (1946)	B	1	298.15	8
	Hamann and Pearse[89] (1952)	B	7	303 to 363	1
	David et al.[90] (1959)	B	11	303 to 403	2
	Titani[68] (1930)	η	7	293 to 393	3
	McCubrey and Singh[91] (1957)	η	8	308 to 445	2
	Lambert et al.[73] (1955)	η	8	308 to 355	3
	Dunlop[78] (1994)	η	1	298.15	2
1-butene	Roper[43] (1940)	B	5	243 to 333	8 to 19
	Pompe and Spurling[48] (1974)	B	7	377 to 523	5 to 7
	Aston et al.[92] (1946)	B	1	298.15	2.5
	McGlashan and Wormald[82] (1964)	B	12	304 to 420	2
	Titani[68] (1930)	η	6	303 to 393	3
cis-2-butene	Roper[43] (1940)	B	9	250 to 343	1.5 to 2
	Lambert et al.[73] (1955)	η	4	323 to 351	2
trans-2-butene	Roper[43] (1940)	B	12	243 to 333	1.5 to 2
	Titani[68] (1930)	η	6	298 to 393	3
	Trautz and Husseini[86] (1934)	η	8	290 to 523	3
	Lambert et al.[73] (1955)	η	8	323 to 351	2
iso-butene	Roper[43] (1940)	B	4	243 to 333	2
	Beattie et al.[93] (1942)	B	6	423 to 548	2
	Titani[68] (1930)	η	6	303 to 393	3

Table 2. Potential Parameters $R_m(T)$, $\varepsilon(T)$, n, and δ_0 at $T = 0$ K and rms Deviation, Equation 5, of C_mH_{2m}, $m < 5$

molecule	$10^{10}R_m(0)$/m	$[\varepsilon(0)/k_B]$/K	n	$10^{12}\delta_0$/m	rms
ethene	4.132 ± 0.001	375.40 ± 0.24	29.03 ± 0.08	4.46 ± 0.30	0.645
propene	4.826 ± 0.003	433.7 ± 0.3	17.1 ± 0.05	4.07 ± 0.10	0.612
cyclopropane	4.623 ± 0.022	491.8 ± 2.4	21.2 ± 1.0	5.50 ± 1.0	0.413
1-butene	5.080 ± 0.006	635.0 ± 1.7	35.2 ± 2.6	2.14 ± 1.0	0.791
cis-2-butene	4.937 ± 0.020	696 ± 14	19.76 ± 0.93	12.2 ± 1.0	0.442
trans-2-butene	5.009 ± 0.010	701.5 ± 2.2	24.9 ± 1.3	7.390 ± 0.003	0.633
iso-butene	4.970 ± 0.001	672.4 ± 2.2	38.3 ± 0.54	1.897 ± 0.001	0.512

$$U(R,T) = \frac{\varepsilon(T)}{n-6}\left[6\left(\frac{R_m(T)}{R}\right)^n - n\left(\frac{R_m(T)}{R}\right)^6\right] \qquad (1)$$

$U(R,T)$ is the intermolecular interaction energy; R is the center-of-mass distance; $R_m(T)$ is the equilibrium distance; $\varepsilon(T)$ the potential well-depth; and n is the repulsive parameter. In our model, the latter one does not depend on the temperature T. As already discussed in detail (see, e.g., ref 32), the temperature dependence of $R_m(T)$ and $\varepsilon(T)$ 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 do not show any temperature dependence.[40] The separation between two molecules is

$$R_m(T) = R_m(T = 0\ \text{K}) + \delta_0 \cdot f(T) \qquad (2)$$

where the term $\delta_0 \cdot f(T)$ 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 Hohm and Zarkova[32] and Stefanov[41] for details). Assuming that the attractive dispersion-interaction does not depend on the temperature, the potential well-depth for the interaction between two equal particles is given by

$$\varepsilon(T) = \varepsilon(0)[R_m(0)/R_m(T)]^6 \qquad (3)$$

Within our model and the considered maximum temperature of 1100 K, this is a reasonable assumption. By using the (n-6) LJTDP, the second pVT virial coefficient B, the viscosity η,

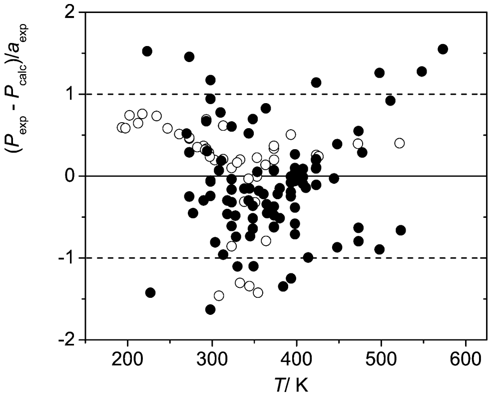

Figure 2. Deviations $P_{exp} - P_{calc}$ between experimental and calculated properties $P = B$ or η for propene, C_3H_6, normalized to their individual experimental uncertainties a_{exp}: ●, second pVT virial coefficients B; ○, viscosities η.

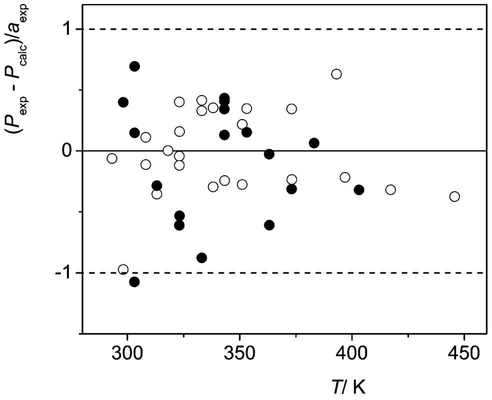

Figure 3. Deviations $P_{exp} - P_{calc}$ between experimental and calculated properties $P = B$ or η for cyclopropane, C_3H_6, normalized to their individual experimental uncertainties a_{exp}: ●, second pVT virial coefficients B; ○, viscosities η.

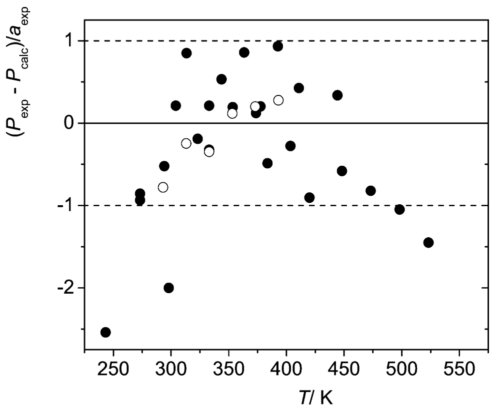

Figure 4. Deviations $P_{exp} - P_{calc}$ between experimental and calculated properties $P = B$ or η for 1-butene, C_4H_8, normalized to their individual experimental uncertainties a_{exp}: ●, second pVT virial coefficients B; ○, viscosities η.

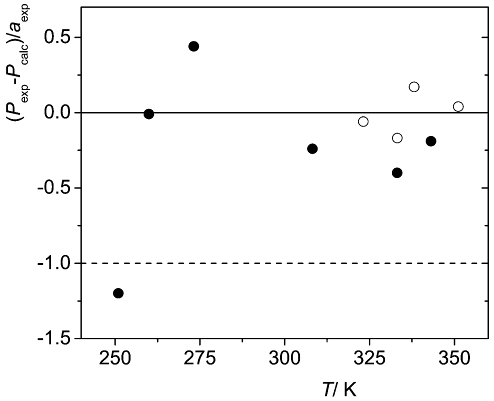

Figure 5. Deviations $P_{exp} - P_{calc}$ between experimental and calculated properties $P = B$ or η for *cis*-2-butene, C_4H_8, normalized to their individual experimental uncertainties a_{exp}: ●, second pVT virial coefficients B; ○, viscosities η.

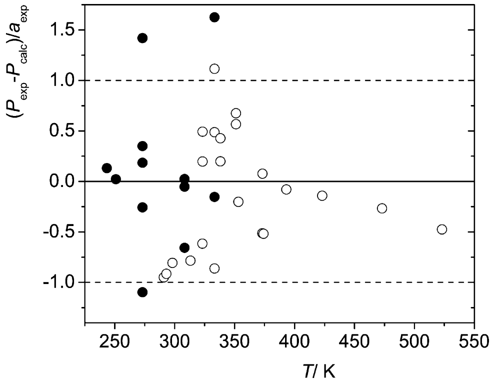

Figure 6. Deviations $P_{exp} - P_{calc}$ between experimental and calculated properties $P = B$ or η for *trans*-2-butene, C_4H_8, normalized to their individual experimental uncertainties a_{exp}: ●, second pVT virial coefficients B; ○, viscosities η.

Table 3. Dimensionless Properties $B^* = B/(\mathrm{cm^3 \cdot mol^{-1}})$, $\eta^* = \eta/(\mu\mathrm{Pa \cdot s})$, and $\rho D^* = \rho D/(10^{-3} \cdot \mathrm{g \cdot m^{-1} \cdot s^{-1}})$ of C_nH_{2n}

	ethene, (C_2H_4)			propene, (C_3H_6)			cyclopropane, (C_3H_6)			1-butene, (C_4H_8)			*cis*-2-butene, (C_4H_8)			*trans*-2-butene, (C_4H_8)			iso-butene, (C_4H_8)		
T/K	*B**	*η**	*ρD**	*B**	*η**	*ρD**	*B**	*η**	*ρD**	*B**	*η**	*ρD**	*B**	*η**	*ρD**	*B**	*η**	*ρD**	*B**	*η**	*ρD**
200	−314.1	7.236	9.445	−793.2	5.894	7.779	−879.4	6.226	8.124	−1693	5.682	7.321	−2277	5.580	7.198	−2151	5.547	7.148	−1800	5.892	7.578
210	−284.7	7.552	9.861	−714.8	6.169	8.154	−789.2	6.498	8.492	−1486	5.914	7.631	−1960	5.813	7.518	−1857	5.776	7.458	−1572	6.133	7.896
220	−259.3	7.867	10.27	−648.3	6.448	8.530	−713.4	6.770	8.860	−1317	6.146	7.940	−1707	6.046	7.838	−1622	6.004	7.767	−1388	6.370	8.213
230	−237.2	8.182	10.69	−591.2	6.728	8.907	−648.8	7.040	9.227	−1177	6.377	8.248	−1501	6.278	8.159	−1431	6.231	8.077	−1237	6.606	8.528
240	−217.9	8.497	11.10	−541.6	7.010	9.284	−593.2	7.310	9.593	−1060	6.607	8.554	−1330	6.509	8.482	−1273	6.457	8.386	−1111	6.842	8.841
250	−200.8	8.811	11.50	−498.3	7.293	9.660	−544.9	7.584	9.958	−960.9	6.836	8.860	−1188	6.741	8.806	−1140	6.684	8.696	−1004	7.077	9.152
260	−185.6	9.124	11.91	−460.0	7.577	10.03	−502.5	7.863	10.33	−875.5	7.063	9.164	−1067	6.977	9.134	−1028	6.912	9.008	−912.9	7.311	9.463
270	−171.9	9.437	12.31	−426.0	7.861	10.41	−465.1	8.141	10.69	−801.5	7.290	9.468	−964.0	7.217	9.465	−932.1	7.142	9.319	−834.4	7.545	9.772
280	−159.6	9.749	12.71	−395.5	8.147	10.78	−431.7	8.416	11.07	−736.9	7.520	9.771	−874.6	7.460	9.800	−848.9	7.373	9.632	−766.2	7.778	10.08
290	−148.5	10.06	13.11	−368.2	8.434	11.16	−401.8	8.689	11.44	−680.0	7.750	10.07	−796.7	7.708	10.14	−776.3	7.606	9.946	−706.2	8.011	10.39
300	−138.4	10.37	13.50	−343.4	8.721	11.54	−374.9	8.964	11.80	−629.5	7.979	10.37	−728.2	7.958	10.48	−712.4	7.840	10.26	−653.3	8.243	10.70
310	−129.1	10.68	13.90	−320.9	9.007	11.91	−350.5	9.240	12.17	−584.4	8.205	10.68	−667.5	8.212	10.82	−655.8	8.075	10.57	−606.2	8.474	11.00
320	−120.6	10.99	14.29	−300.4	9.289	12.29	−328.2	9.522	12.53	−543.9	8.431	10.98	−613.5	8.469	11.16	−605.3	8.312	10.89	−564.1	8.706	11.31
330	−112.8	11.30	14.68	−281.6	9.570	12.66	−307.9	9.807	12.89	−507.4	8.658	11.27	−565.0	8.728	11.51	−560.0	8.550	11.20	−526.2	8.937	11.61
340	−105.5	11.60	15.06	−264.2	9.851	13.03	−289.3	10.09	13.25	−474.3	8.887	11.57	−521.4	8.989	11.85	−519.1	8.789	11.52	−491.9	9.169	11.91
360	−92.6	12.21	15.82	−233.4	10.43	13.75	−256.2	10.65	13.98	−416.6	9.345	12.16	−445.9	9.516	12.54	−448.3	9.270	12.14	−432.4	9.630	12.52
380	−81.3	12.80	16.56	−206.9	11.02	14.48	−227.8	11.21	14.71	−368.0	9.800	12.75	−382.8	10.05	13.24	−389.1	9.754	12.77	−382.5	10.09	13.11
400	−71.4	13.40	17.30	−183.7	11.58	15.19	−203.1	11.76	15.43	−326.5	10.25	13.33	−329.4	10.59	13.94	−338.9	10.24	13.39	−340.0	10.55	13.71
420	−62.6	13.98	18.03	−163.4	12.12	15.90	−181.4	12.33	16.13	−290.6	10.70	13.91	−283.5	11.13	14.62	−295.7	10.73	14.02	−303.5	11.01	14.30
440	−54.8	14.56	18.75	−145.3	12.65	16.60	−162.1	12.89	16.83	−259.3	11.16	14.47	−243.5	11.69	15.29	−258.1	11.22	14.63	−271.7	11.47	14.88
460	−47.8	15.13	19.45	−129.1	13.20	17.28	−145.0	13.44	17.52	−231.7	11.61	15.03	−208.5	12.23	15.96	−225.1	11.70	15.23	−243.9	11.92	15.45
480	−41.4	15.68	20.13	−114.6	13.74	17.95	−129.5	13.98	18.21	−207.3	12.05	15.59	−177.4	12.74	16.63	−195.8	12.18	15.82	−219.2	12.38	16.02
500	−35.6	16.23	20.81	−101.4	14.27	18.60	−115.6	14.52	18.90	−185.4	12.49	16.15	−149.6	13.26	17.26	−169.6	12.66	16.41	−197.2	12.83	16.58
520	−30.3	16.77	21.47	−89.6	14.78	19.23	−102.9	15.05	19.56	−165.7	12.93	16.69	−124.5	13.77	17.87	−146.0	13.13	16.99	−177.4	13.28	17.14
540	−25.5	17.30	22.12	−78.5	15.27	19.85	−91.3	15.57	20.21	−147.9	13.36	17.22	−101.8	14.25	18.45	−124.6	13.58	17.55	−159.6	13.72	17.70
560	−21.0	17.82	22.76	−68.5	15.75	20.47	−80.69	16.09	20.84	−131.7	13.79	17.74	−81.1	14.71	19.01	−105.2	14.03	18.08	−143.4	14.16	18.24
580	−16.9	18.34	23.39	−59.2	16.22	21.08	−70.9	16.60	21.46	−116.9	14.21	18.26	−62.1	15.14	19.56	−87.3	14.46	18.60	−128.6	14.59	18.78
600	−13.0	18.84	24.00	−50.6	16.68	21.68	−61.8	17.10	22.07	−103.3	14.63	18.76	−44.5	15.55	20.07	−70.9	14.89	19.11	−115.1	15.02	19.30
640	−6.10	19.80	25.20	−35.2	17.58	22.81	−45.6	18.05	23.26	−79.1	15.44	19.75	−13.0	16.31	20.98	−41.5	15.68	20.08	−91.1	15.87	20.32
680	−0.02	20.73	26.35	−21.8	18.44	23.89	−31.4	18.96	24.40	−58.3	16.22	20.71	14.6	16.95	21.77	−8.73	16.42	20.97	−70.6	16.70	21.32
720	5.37	21.63	27.45	−9.96	19.26	24.91	−18.9	19.82	25.47	−40.2	16.99	21.62	39.1	17.48	22.47	6.51	17.08	21.78	−52.7	17.49	22.30
760	10.2	22.48	28.50	0.58	20.01	25.89	−7.82	20.63	26.47	−24.2	17.72	22.49	61.2	17.94	23.06	26.6	17.68	22.51	−37.0	18.26	23.23
800	14.5	23.30	29.51	10.0	20.72	26.83	2.16	21.40	27.42	−9.93	18.41	23.33	81.4	18.31	23.54	44.8	18.22	23.18	−23.1	19.01	24.12
840	18.5	24.08	30.48	18.6	21.41	27.72	11.2	22.11	28.32	2.85	19.08	24.13	100.0	18.60	23.93	61.4	18.69	23.77	−10.6	19.73	24.98
880	22.1	24.84	31.41	26.4	22.06	28.58	19.4	22.78	29.17	14.4	19.71	24.91	117.3	18.83	24.22	76.7	19.11	24.31	0.63	20.43	25.81
920	25.4	25.55	32.31	33.5	22.68	29.39	27.0	23.41	29.98	24.9	20.32	25.64	133.6	19.01	24.45	90.9	19.48	24.77	10.8	21.09	26.61
960	28.5	26.24	33.17	40.1	23.27	30.15	33.9	23.99	30.73	34.6	20.89	26.34	149.0	19.15	24.63	104.1	19.80	25.19	20.1	21.73	27.39
1000	31.3	26.90	34.00	46.1	23.82	30.88	40.4	24.54	31.43	43.4	21.44	27.00	163.6	19.25	24.76	116.6	20.08	25.54	28.7	22.34	28.13

and the diffusion coefficient *D* can be calculated via standard formulas which are given, e.g., by Hirschfelder et al.[30] or more condensed by Zarkova et al.,[35] where the case of binary mixtures is also considered.

Procedure and Input Data. To obtain the factor *f*(*T*) of eq 2, the vibrational partition function is calculated in the harmonic oscillator approximation. The vibrational fundamental frequencies are taken from the literature.[42]

The potential parameters of the (*n*-6) LJTDP of each C_mH_{2m} molecule were determined by minimizing the sum *F* of the squared deviations between experimentally measured (index "exp") and calculated (index "calc") thermophysical properties normalized to their relative experimental error a_{exp}

$$F = \sum_i^{N_\eta}\left[\frac{\ln\left(\frac{\eta_{\mathrm{exp}}}{\eta_{\mathrm{calc}}}\right)}{a_{\eta\mathrm{exp}}}\right]^2 + \sum_i^{N_B}\left[\frac{\ln\left(\frac{B_{\mathrm{exp}}}{B_{\mathrm{calc}}}\right)}{a_{B\mathrm{exp}}}\right]^2 + \sum_i^{N_{\rho D}}\left[\frac{\ln\left(\frac{\rho D_{\mathrm{exp}}}{\rho D_{\mathrm{calc}}}\right)}{a_{\rho D\mathrm{exp}}}\right]^2 \tag{4}$$

As input data, we have generally used N_η viscosities η, N_B second *pVT* virial coefficients *B*, and $N_{\rho D}$ diffusion coefficients

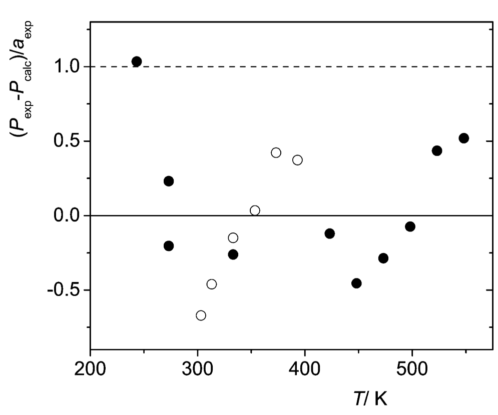

Figure 7. Deviations $P_{\mathrm{exp}} - P_{\mathrm{calc}}$ between experimental and calculated properties $P = B$ or η for iso-butene, C_4H_8, normalized to their individual experimental uncertainties a_{exp}: ●, second *pVT* virial coefficients *B*; ○, viscosities η.

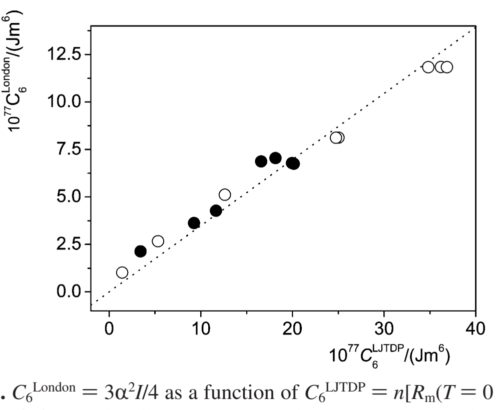

Figure 8. $C_6^{\mathrm{London}} = 3\alpha^2 I/4$ as a function of $C_6^{\mathrm{LJTDP}} = n[R_m(T = 0\ \mathrm{K})]^6\varepsilon(T = 0\ \mathrm{K})/(n\text{-}6)$ for, ●, the alkenes ethene, cyclopropane, propene, iso-butene, 1-butene, *cis*-2-butene, *trans*-2-butene, and, ○, the alkanes CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10}, $C(CH_3)_4$, *n*-C_5H_{12}, and *i*-C_5H_{12}. The compounds are listed by increasing value of C_6^{LJTDP}. The dotted curve is the linear least-squares fit which goes through zero.

Table 4. Coefficients for $R_m(T)$ According to Equation 6[a]

molecule	$10^{10}\ A_1$/m	B_1/K	$10^{10}\ A_2$/m	B_2/K	$10^{14}\Delta R_m(T)$/m
ethene	0.55213 ± 0.00631	1428.9 ± 4.6	1.2309 ± 0.0130	340.7 ± 31.7	0.92
propene	0.3848 ± 0.0119	498.3 ± 9.0	2.2622 ± 0.0294	2087 ± 29	16
cyclopropane	1.3056 ± 0.0076	1310.4 ± 2.1	2.2213 ± 0.0159	3041 ± 19	10
1-butene	0.34329 ± 0.00594	558.5 ± 4.9	1.6150 ± 0.0126	2025 ± 18	5.2
cis-2-butene	1.7185 ± 0.0559	716.5 ± 10.2	8.908 ± 0.108	2334.1 ± 32	39
trans-2-butene	0.9193 ± 0.0273	547.9 ± 8.8	5.4840 ± 0.070	2181 ± 29	32
iso-butene	0.29120 ± 0.00837	549.13 ± 8.46	1.48623 ± 0.0189	2135 ± 30	9.4

[a] $\Delta R_m(T)$ denotes the standard deviation of the fit.

Table 5. Fit Parameters According to Equations 7 and 8 for the Alkenes and Cycloalkanes C_nH_{2n}, $n < 5$[a]

property	fit parameter	ethene	propene	cyclopropane	1-butene	*cis*-2-butene	*trans*-2-butene	iso-butene
B	P_1	98.65 ± 0.35	191.81 ± 0.46	190.47 ± 0.71	237.12 ± 0.84	601.3 ± 7.5	404.2 ± 6.8	214.4 ± 1.1
	$10^{-4}P_2$	−7.017 ± 0.046	−15.222 ± 0.060	−15.54 ± 0.12	−18.86 ± 0.13	−55.51 ± 0.99	−30.7 ± 1.1	−17.64 ± 0.16
	$10^{-6}P_3$	4.11 ± 0.17	10.50 ± 0.23	10.09 ± 0.51	6.08 ± 0.53	150.8 ± 3.8	39.0 ± 4.6	3.30 ± 0.63
	$10^{-9}P_4$	−1.320 ± 0.020	−3.893 ± 0.026	−3.56 ± 0.14	−4.12 ± 0.0.13	−31.01 ± 0.43	−9.37 ± 0.91	−3.55 ± 0.15
	P_5	0.0 (fixed)	0.0 (fixed)	11.3 ± 1.3	39.22 ± 0.84	0.0 (fixed)	36.3 ± 2.8	47.46 ± 0.95
	$\Delta B/(\text{cm}^3\cdot\text{mol}^{-1})$	0.23	0.31	0.19	0.30	5.04	2.80	0.50
η	P_1	0.018 ± 0.052	−0.88 ± 0.10	0.581 ± 0.067	1.109 ± 0.025	2.99 ± 0.28	2.816 ± 0.071	1.508 ± 0.030
	10^2P_2	3.805 ± 0.029	3.519 ± 0.057	2.689 ± 0.040	2.224 ± 0.015	0.02 ± 0.21	0.443 ± 0.055	2.045 ± 0.023
	10^5P_3	−1.143 ± 0.048	−0.946 ± 0.093	0.686 ± 0.071	0.4011 ± 0.026	8.12 ± 0.55	5.99 ± 0.14	1.028 ± 0.059
	10^8P_4	0.031 ± 0.024	−0.096 ± 0.045	−0.988 ± 0.039	−0.596 ± 0.014	−9.77 ± 0.58	−7.02 ± 0.15	−1.360 ± 0.062
	$10^{11}P_5$	-	-	-	-	3.24 ± 0.21	2.314 ± 0.054	0.370 ± 0.023
	$10^3\Delta\eta/(\mu\text{Pa}\cdot\text{s})$	34	67	35	13	80	20	8.6
ρD	P_1	0.110 ± 0.031	−1.060 ± 0.76	0.153 ± 0.067	0.752 ± 0.029	2.17 ± 0.29	2.170 ± 0.054	1.278 ± 0.019
	10^2P_2	5.013 ± 0.017	4.668 ± 0.043	4.007 ± 0.040	3.364 ± 0.017	1.43 ± 0.22	1.758 ± 0.041	3.114 ± 0.014
	10^5P_3	−1.875 ± 0.029	−1.500 ± 0.070	−0.166 ± 0.071	−0.405 ± 0.031	7.03 ± 0.57	4.88 ± 0.11	0.425 ± 0.037
	10^8P_4	0.254 ± 0.014	0.029 ± 0.035	−0.721 ± 0.039	−0.337 ± 0.017	−9.29 ± 0.60	−6.49 ± 0.11	−1.260 ± 0.039
	$10^{11}P_5$	-	-	-	-	3.08 ± 0.22	2.193 ± 0.041	0.407 ± 0.014
	$10^5\Delta\rho D\ /(\text{g}\cdot\text{m}^{-1}\cdot\text{s}^{-1})$	2.0	4.1	3.5	1.5	8.3	1.5	0.53

[a] ΔP ($P = B$, η, or ρD) denotes the standard deviation of the fit.

ρD, whereas the calculations are performed with the parametrized LJTDP, eq 1. The final potential parameters (PP) are obtained by minimizing the root-mean-square (rms) deviation

$$\text{rms} = \sqrt{F/M} \tag{5}$$

$M = N_\eta + N_B + N_D$ is the total number of the experimental input data which are given in Table 1. All of the viscosities η were used as given in the original sources. However, in some cases we are forced to assume reasonable experimental uncertainties (see Table 1). It is worth mentioning that especially in the case of the experimentally determined viscosities of the small alkenes the interested reader should consult the original sources and not rely on commonly used data compilations such as the Landolt−Börnstein tables[94] or the DIPPR801[95] database. We found some erroneous entries and misleading references for η. In the case of the second virial coefficient B, the number of experimental data points and their uncertainties as given in the original sources is sometimes different from the entries in Table 1. Especially in the case of ethene and propene where a large number of experimentally determined second virial coefficients B are available, systematic deviations and outliers can be detected quite easily. For ethene, the experimental results reported by Lee and Edmister[46] (below 348 K) and Häusler and Kerl[61] (below 282 K) are much more negative than the rest of the experimental data. The error bars do not overlap, and therefore, these data were not taken into account. For cyclopropane and the butenes, only few experimental data on the second virial coefficient are available. Systematic deviations are hardly detectable in these cases. All data were used as given by the authors except for the results on 1-butene which are obtained from heat capacity and vapor pressure measurements by Aston et al.[92] Here we found that too many assumptions prevent extraction of reliable B-data from these kinds of experiments. The final potential parameters at $T = 0$ K and the root-mean-square deviations rms are given in Table 2.

Our goal was to present a complete study on the molecules C_mH_{2m}. However, no experimental thermophysical input data which can be used in our minimization procedure were found in the case of cyclobutane.

Results and Discussion

Potential Parameters. As can be seen in Table 2, the obtained potential parameters enable us to reproduce the experimental input data within their experimental uncertainty, rms ≤ 1 a_{exp}. This is also illustrated in the deviation plots (Figures 1 to 7). Most of the experimental data are reproduced well within their experimental uncertainties a_{exp}. Except for 1-butene, no systematic trends can be observed. The deviations for B and η are distributed symmetrically around the zero line. In the case of 1-butene, a slightly parabolic distribution of the deviations is observed (see Figure 4).

As was observed earlier for the alkanes C_mH_{2m+2}[31,32] and perfluoroalkanes C_mF_{2m+2}[33] $R_m(T = 0\ \text{K})$ and $\varepsilon(T = 0\ \text{K})$ of the alkenes and cyclopropane increase with increasing size of the molecules. Also comparable to our findings for C_mH_{2m+2} and C_mF_{2m+2}, the repulsive parameter n does not follow a simple trend and varies between 17.1 (propene) and 38.3 (iso-butene). It is, therefore, instructive to look at the dispersion-interaction energy constant C_6, which in the case of the LJTDP is given by $C_6^{\text{LJTDP}} = n[R_m(T = 0\ \text{K})]^6\varepsilon(T = 0\ \text{K})/(n\text{-}6)$. For the alkanes, we observed a very good linear correlation between C_6^{LJTDP} and the exact C_6 which can be obtained from dipole-oscillator strength distributions (DOSDs). In the case of the alkenes, the exact C_6 value is not always available. To get a consistent picture, we used the London approximation $C_6^{\text{London}} = 3\alpha^2I/4$, where α is the electronic part of the static dipole polarizability volume and I is the ionization potential. Figure 8 shows a plot of C_6^{London} against C_6^{LJTDP} for the alkanes C_mH_{2m+2} and the alkenes (including cyclopropane) C_mH_{2m}. The alkenes show the same regular behavior, and a linear dependence can also be observed in this case.

Thermophysical Properties. The potential parameters of the (n-6) LJTDP are used to calculate the second pVT virial coefficient B, the viscosity η,and the diffusion coefficient ρD of the pure low-density alkenes. The results are given in Table 3.

Our obtained $R_m(T)$, eq 2, is fitted to

$$R_m(T) = R_m(0) + A_1 \exp(-B_1/T) + A_2 \exp(-B_2/T) \quad (6)$$

The fitting constants A_1, A_2, B_1, and B_2 are given in Table 4. By using eq 3, they allow for a direct calculation of $\varepsilon(T)$.

To allow for a fast calculation of some thermophysical properties $P(T)$ of the low-density gaseous alkenes, the dimensionless quantities $P(T) = \eta/(\mu\text{Pa}\cdot\text{s})$ and $P(T) = \rho D/(10^{-3}\cdot\text{g}\cdot\text{m}^{-1}\cdot\text{s}^{-1})$ are fitted to a polynomial in powers of the temperature T of the form

$$P(T) = \sum_{i=1}^{5} P_i (T/\text{K})^{i-1} \quad (7)$$

whereas we found that the dimensionless second pVT virial coefficient $P(T) = B(T)/(\text{cm}^3\cdot\text{mol}^{-1})$ can best be represented by

$$P(T) = \sum_{i=1}^{4} P_i (T/\text{K} - P_5)^{1-i} \quad (8)$$

The so obtained fit parameters are given in Table 5.

We note that our results present the first systematic study of an effective intermolecular–interaction potential of the butenes. It has become clear that due to a severe lack of experimental thermophysical data our results are very useful in predicting some of the thermophysical properties of these important substances. However, one has to bear in mind that with more experimental input the predictive power of our results can be increased considerably.

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