Correlations

Perfluorinated *n*-Alkanes C_mF_{2m+2} ($m < 7$): Second *pVT*-Virial Coefficients, Viscosities, and Diffusion Coefficients Calculated by Means of an (*n*-6) Lennard-Jones Temperature-Dependent Potential

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The perfluorinated *n*-alkanes C_mF_{2m+2} ($m = 1$ to 6) are widely used and expensive substances that are not only of technological interest for the semiconductor industry but also powerful greenhouse gases having an important impact on the atmosphere. This paper presents tables with recommended thermophysical data in the temperature range (200 to 1000) K at pressures of ≤ 0.1 MPa. Second *pVT*-virial coefficients B, viscosities η, and diffusion coefficients D are calculated by means of an (*n*-6) Lennard-Jones temperature-dependent potential. The potential parameters, equilibrium distance, and potential well depth 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. New tables of the harmonic vibrational frequencies of n-C_4F_{10}, n-C_5F_{12}, and n-C_6F_{14}, which are required as input parameters in the course of the calculations, are also presented.

Introduction

Recently, interest in the transport properties of the perfluorocarbons (PFCs) has grown noticeably. The reason is not only the wide application of these gases in semiconductor and chemical vapor deposition manufacturing but also the fact of their accumulation in the atmosphere. The global warming potential of the perfluoroalkanes C_mF_{2m+2} is almost as high as that of CO_2, and this is why they have been included in the Kyoto protocol as greenhouse gases.[1]

In particular, recent research devoted to the perfluoroalkanes C_mF_{2m+2} spans wide areas such as experimental[2] and theoretical[3] studies on the production of fluorocarbon thin films, as well as plasma etching[4] and hot atom reactions occurring at the surface of spacecrafts flying in low Earth orbits.[5] More closely related to our present investigations are studies that deal with the intermolecular interaction potential of pure perfluoroalkanes or of binary mixtures of C_mF_{2m+2} with other small molecules.[6−10] Some of them are aimed at getting detailed information about the binary interactions only,[9] whereas others also intend to predict liquid-phase properties via molecular dynamics simulations.[7,8] It is also widely known that the highly fluorinated compounds exhibit a unique sorption and partition behavior.[11] Despite their importance, however, only a very limited number of their low-density thermophysical properties are available, especially for the higher homologues of C_mF_{2m+2} with $m > 2$. To extend our studies of the gas-phase thermophysical properties such as the second *pVT*-virial coefficient $B(T)$, the second speed-of-sound virial coefficient $\beta(T)$, the viscosity $\eta(T)$, and the diffusion coefficient $D(T)$ of the perfluorinated *n*-alkanes, we rely on our recently developed model of a Lennard-Jones (*n*-6) temperature-dependent potential, (*n*-6) LJTDP. Hitherto the (*n*-6) LJTDP has been very successfully applied to small- and medium-sized spherically shaped molecules such as CH_4, CF_4, and $C(CH_3)_4$[12] and also to nonspherical species such as Cl_2 and the *n*-alkanes C_mH_{2m+2}, $m < 6$.[13,14] We are presenting new results for C_mF_{2m+2} ($m > 1$), but for the sake of completeness some of the hitherto obtained data on CF_4[12] are repeated here.

Theoretical Section

Potential Model. The (*n*-6) LJTDP is a spherical potential with explicitly temperature-dependent potential parameters:

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

$U(R,T)$ is the intermolecular interaction energy, R is the center-of-mass distance, $R_m(T)$ is the equilibrium distance, $\epsilon(T)$ is the potential well depth, and n is the repulsive parameter. In our model n does not depend on the temperature T. As already discussed in detail (see, e.g., ref 13), the temperature dependence of $R_m(T)$ and $\epsilon(T)$ is due to the vibrational excitation of the molecules. Therefore, in our model the potential parameters (PP) of, for example, the noble gases argon, krypton, and xenon do not show any temperature dependence.[15] The separation between two molecules is

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

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10.1021/je700182n CCC: \$37.00

Table 1. Experimental Input Data

molecule	reference	property	no., N_i, of input data	ΔT K	rel exptl error, a_{exptl} %
C_2F_6	Pace and Aston[21] (1948)	B	9	180 to 298	2.5 to 8.5
	Bell et al.[22] (1992)	B	3	290 to 310	1
	Di Nicola et al.[23] (2004)	B	7	283 to 346	0.7 to 1.1
	Hurly[24] (1999)	β	10	215 to 475	1
	Hurly et al.[25] (2003)	β	5	225 to 375	1 to 2.5
	Hurly et al.[25] (2003)	η	7	225 to 375	2
	McCoubrey and Singh[26] (1960)	η	8	291 to 456	3
	Dunlop[27] (1994)	η	1	298.15	1
C_3F_8	Dantzler and Knobler[28] (1969)	B	2	323 to 373	7 to 10
	Pace and Plaush[29] (1967)	B	1	236	8
	Brown[30] (1963)	B	7	233 to 373	3 to 8
	Lapardin[31] (1983)	η	10	272 to 421	3
n-C_4F_{10}	Tripp and Dunlap[32] (1962)	B	6	283 to 323	5 to 10
	Dantzler and Knobler[28] (1969)	B	2	323 to 373	10
	Brown and Mears[33] (1958) as cited by ref 32	B	3	283 to 323	5 to 10
	Matheson[34] (1974)	η	6	273 to 573	10 to 20
n-C_5F_{12}	Garner and McCoubrey[35] (1959)	B	6	307 to 383	1 to 2.5
	Dantzler and Knobler[28] (1969)	B	2	323 to 373	10
	McCoubrey and Singh[26] (1960)	η	6	296 to 471	3
n-C_6F_{14}	Garner and McCoubrey[35] (1959)	B	3	330 to 351	5
	Cecil[36] (1964)	B	3	303 to 341	5
	Taylor and Reed[37] (1970)	B	7	341 to 451	1 to 5
	McCoubrey and Singh[26] (1960)	η	4	296 to 471	3

Table 2. Potential Parameters $R_m(T)$, $\epsilon(T)$, n, and δ_0 at $T = 0$ K and RMS Deviation, Equation 5, of the n-Perfluoroalkanes C_mF_{2m+2}, $m < 7$

	$10^{10}R_m(T = 0\text{ K})$	$[\epsilon(T = 0\text{ K})/k]$		$10^{12}\delta_0$	
molecule	m	K	n	m	RMS
CF_4[a]	4.329 ± 0.002	328.4 ± 1.1	52.71 ± 0.63	1.29 ± 0.03	0.701
C_2F_6	5.09 ± 0.41	470.511 ± 0.031	132.9 ± 1.2	0.31 ± 0.10	1.024
C_3F_8	5.266 ± 0.018	666.4 ± 5.6	32.6 ± 1.0	2.05 ± 0.10	0.366
n-C_4F_{10}	5.193 ± 0.023	972.1 ± 8.7	12.00 ± 0.31	2.90 ± 0.10	0.584
n-C_5F_{12}	6.0466 ± 0.0080	974.6 ± 2.3	39.58 ± 0.59	1.32 ± 0.10	0.396
n-C_6F_{14}	6.286 ± 0.025	1080 ± 12	46.9 ± 1.7	0.82 ± 0.10	0.388

[a] Reference 12.

where the term $\delta_0 \times f(T)$ 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 13 and 16 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

$$\epsilon(T) = \epsilon(0)[R_m(0)/R_m(T)]^6 \tag{3}$$

Within our model and the considered maximum temperature of 1000 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 one is dealing with very high temperatures at which, for example, blackbody radiation effects become important.[17,18]

Procedure and Input Data. To obtain the factor $f(T)$ of eq 2, the vibrational partition function is calculated in the harmonic oscillator approximation. In the case of CF_4, C_2F_6, and C_3F_8 the vibrational fundamental frequencies are taken from the literature.[19,20] Due to a severe lack of experimental and theoretical data the vibrational frequencies of C_4F_{10}, C_5F_{12}, and C_6F_{14} are calculated in this work (see next section).

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

$$F = \sum_i^{N_\eta}\left[\frac{\ln\left(\dfrac{\eta_{\text{exptl}}}{\eta_{\text{calcd}}}\right)}{a_{\eta,\text{exptl}}}\right]^2 + \sum_i^{N_B}\left[\frac{\ln\left(\dfrac{B_{\text{exptl}}}{B_{\text{calcd}}}\right)}{a_{B,\text{exptl}}}\right]^2 + \sum_i^{N_\beta}\left[\frac{\ln\left(\dfrac{\beta_{\text{exptl}}}{\beta_{\text{calcd}}}\right)}{a_{\beta,\text{exptl}}}\right]^2 \tag{4}$$

As input data we have generally used N_η viscosities η, N_B second pVT-virial coefficients B, and N_β second acoustic virial coefficients β, whereas the calculations are performed with the parametrized LJTDP, eq 1. All of the experimental input data for C_mF_{2m+2}, $1 < m < 7$, are given in Table 1; in the case of CF_4 the data are already summarized by Zarkova and Hohm[12] and are not repeated here. After inspection of the experimental data given by the various authors, we have realized that not all of them can be used in our minimization procedure. We have identified outliers as well as experimental uncertainties that are obviously too small. In the case of n-C_6F_{14} we have not used B given by Garner and McCoubrey[35] at $T = 307.7$ K, 372.3 K, and 383.9 K as well as B given by Cecil[36] at $T = 351.3$ K. The uncertainty of all viscosities given by McCoubrey and Singh[21] has been set to 3%, as was recommended by Vogel.[38]

The final potential parameters (PP) are obtained by minimizing the root-mean-square (RMS) deviation

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

where $M = N_\eta + N_B + N_\beta$ is the number of all experimental input data. The final PP at $T = 0$ K and the RMS deviation are given in Table 2.

Frequency Calculations. Due to a lack of experimental and theoretical data we computed the harmonic vibration wave-

Table 3. Calculated Harmonic Vibration Wavenumbers ω_r and Integrated Absorption Coefficients *A* of the Perfluorocarbons *n*-C_4F_{10}, *n*-C_5F_{12}, and *n*-C_6F_{14} in the Linear Configuration

molecule:	*n*-C_4F_{10}		*n*-C_5F_{12}		*n*-C_6F_{14}	
conformer:	linear		linear		linear	
method:	B3LYP		B3LYP		B3LYP	
basis set:	6-31G(d)		6-31G(d)		6-31G(d)	
	ω_r	*A*	ω_r	*A*	ω_r	*A*
	cm^{-1}	$km \cdot mol^{-1}$	cm^{-1}	$km \cdot mol^{-1}$	cm^{-1}	$km \cdot mol^{-1}$
	26.39	0.00	31.65	0.00	26.24	0.00
	55.96	0.00	46.48	0.00	42.25	0.00
	66.11	0.01	59.25	0.02	46.51	0.00
	122.98	0.00	62.36	0.04	55.46	0.05
	184.50	0.06	103.68	0.31	63.99	0.02
	201.67	4.49	173.92	0.13	90.69	0.20
	234.13	0.00	180.00	0.02	143.50	0.06
	234.18	0.03	200.72	4.94	170.66	0.02
	285.60	6.10	221.42	0.23	198.11	5.53
	288.07	0.01	244.60	0.00	200.42	0.15
	323.95	0.01	245.22	0.14	217.39	0.64
	328.71	0.06	288.11	0.63	230.66	0.11
	359.14	0.02	289.08	7.83	250.47	0.14
	376.20	0.00	316.53	0.03	252.11	0.01
	416.01	1.78	320.00	0.09	286.56	9.48
	499.75	1.07	352.15	0.00	290.53	0.03
	518.53	12.30	365.94	0.08	310.36	0.04
	536.78	0.03	377.48	0.01	313.45	0.22
	579.38	1.53	389.61	1.21	344.16	0.01
	587.50	20.36	461.28	0.41	360.79	0.11
	615.92	1.35	518.31	17.59	368.88	0.39
	687.22	0.28	528.16	8.72	371.30	0.79
	721.85	86.67	531.91	0.77	377.51	0.02
	762.28	0.16	576.29	3.55	432.92	0.47
	909.01	168.49	592.64	1.01	494.54	1.11
	1127.28	2.54	604.27	13.92	517.95	28.51
	1166.58	180.30	634.56	26.78	527.84	0.61
	1211.42	50.15	702.09	2.29	549.27	8.39
	1211.97	3.29	718.19	121.92	560.17	15.61
	1241.18	0.97	755.17	1.88	595.31	1.40
	1251.92	384.06	838.62	110.87	604.80	12.53
	1264.95	34.25	1060.49	3.59	612.75	0.45
	1274.80	710.87	1147.10	45.21	653.20	76.73
	1321.02	0.48	1165.96	137.33	710.94	141.45
	1324.93	281.60	1200.80	6.01	711.05	0.53
	1395.00	0.49	1207.44	4.71	749.83	0.54
			1230.18	415.06	797.38	54.96
			1231.96	145.96	985.97	0.32
			1257.45	96.85	1120.29	87.99
			1260.85	9.16	1151.90	10.20
			1277.69	718.57	1170.65	212.91
			1282.18	98.57	1198.62	0.07
			1310.80	107.59	1201.33	55.78
			1352.02	119.65	1221.68	91.13
			1391.00	3.47	1226.14	82.68
					1231.87	64.92
					1239.10	267.33
					1265.41	95.04
					1273.02	737.54
					1283.34	156.97
					1288.91	96.42
					1331.10	0.69
					1351.29	191.94
					1391.84	0.91

numbers ω_r for *n*-C_4F_{10}, *n*-C_5F_{12}, and *n*-C_6F_{14} by gradient-corrected density functional theory using the Gaussian '03W[39] suite of programs. We used the three-parameter Becke−Lee−Yang−Parr (B3LYP) hybrid functional[40,41] with the double-ζ polarized 6-31G(d) basis set. This methodology reliably reproduces experimental structural, thermochemical, and spectroscopic data for a broad range of compounds.[42,43] The molecular geometries were optimized to yield minimal energy over the conformational space. The published experimental geometries of smaller perfluoroalkanes, CF_4, C_2F_6, and C_3F_8,[20] are reproduced by this methodology with a deviation of less than 1 pm for the bond lengths and 1 % for the bond angles. Harmonic vibrational frequencies were subsequently computed at these fully optimized geometries using the same level of theory. Table 3 illustrates the calculations and gives the necessary information about our original results for *n*-C_4F_{10}, *n*-C_5F_{12}, and *n*-C_6F_{14} of the harmonic vibration wavenumbers ω_r and the integrated absorption coefficient *A* of each mode.

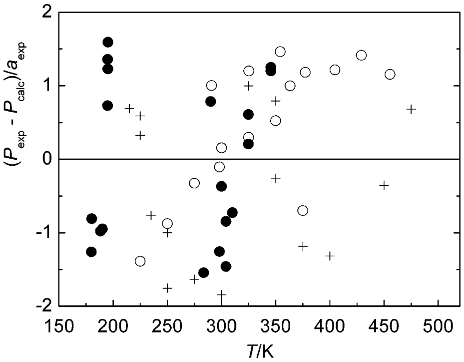

Figure 1. Deviations $P_{exptl} - P_{calcd}$ between experimental and calculated properties $P = B$, η, or β for C_2F_6 normalized to their individual experimental uncertainties a_{exptl}: ●, second *pVT*-virial coefficients *B*; ○, viscosities η; +, second acoustic virial coefficients β.

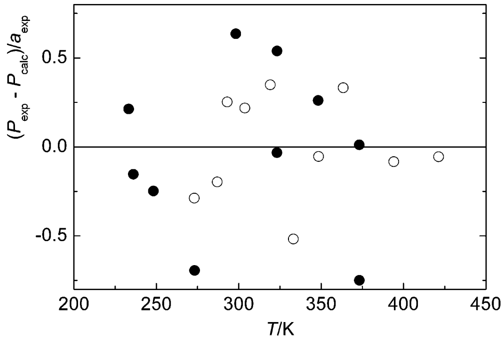

Figure 2. Deviations $P_{exptl} - P_{calcd}$ between experimental and calculated properties $P = B$ or η for C_3F_8 normalized to their individual experimental uncertainties a_{exptl}: ●, second *pVT*-virial coefficients *B*; ○, viscosities η.

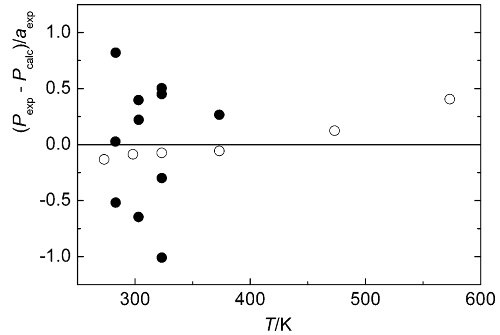

Figure 3. Deviations $P_{exptl} - P_{calcd}$ between experimental and calculated properties $P = B$ or η for *n*-C_4F_{10} normalized to their individual experimental uncertainties a_{exptl}: ●, second *pVT*-virial coefficients *B*; ○, viscosities η.

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 $\leq 1\ a_{exptl}$. This is illustrated in Figures 1 to 5. Except for C_2F_6, all of the measured data are reproduced well within their experimental uncertainties a_{exptl}. In the case of C_2F_6 we found only 56 % within 1 a_{exptl}. Although the deviations for *B* and β are distributed symmetrically around the zero line, a small system-

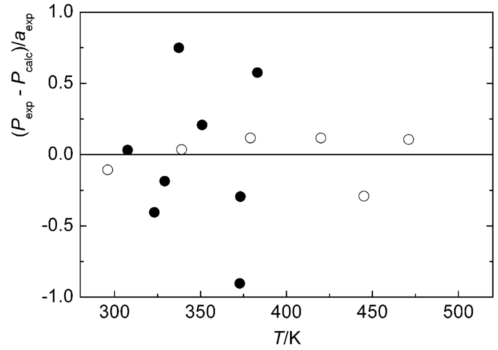

Figure 4. Deviations $P_{exptl} - P_{calcd}$ between experimental and calculated properties $P = B$ or η for n-C_5F_{12} normalized to their individual experimental uncertainties a_{exptl}: ●, second *pVT*-virial coefficients *B*; ○, viscosities η.

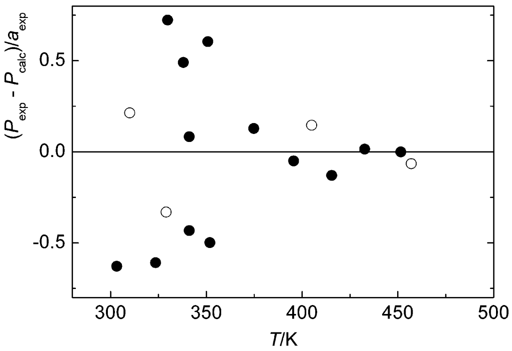

Figure 5. Deviations $P_{exptl} - P_{calcd}$ between experimental and calculated properties $P = B$ or η for n-C_6F_{14} normalized to their individual experimental uncertainties a_{exptl}: ●, second *pVT*-virial coefficients *B*; ○, viscosities η.

atic trend can be observed for η. In the case of the other perfluoroalkanes no such trend is observed, which might be due to the small number of experimental input data, however.

As was observed earlier for the alkanes C_mH_{2m+2}[13,14] $R_m(T = 0\ K)$ and $\epsilon(T = 0\ K)$ of the perfluoroalkanes increase with increasing size of the molecules. The only exception is n-C_4F_{10}, for which $R_m(T = 0\ K)$ is too small and $\epsilon(T = 0\ K)$ is too large. Also comparable to our findings for the alkanes C_mH_{2m+2},[13,14] the repulsive parameter *n* does not follow a simple trend and varies between 12.00 (n-C_4F_{10}) and 132.9 (C_2F_6). It is, therefore, instructive to look at the dispersion−interaction energy constant C_6, which in the case of the LJTDP is given by $C_6^{LJTDP} = n[R_m(T = 0\ K)]^6\epsilon(T = 0\ K)/(n\text{-}6)$. 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).[13] In the case of the perfluoroalkanes the exact C_6 value is available for only CF_4. To get a consistent picture we used the London approximation $C_6 \approx C_6^{London} = 3\alpha^2I/4$, where α is the electronic part of the static dipole polarizability volume[44,45] and *I* is the ionization potential.[46] Figure 6 shows a plot of C_6^{London} against C_6^{LJTDP} for the

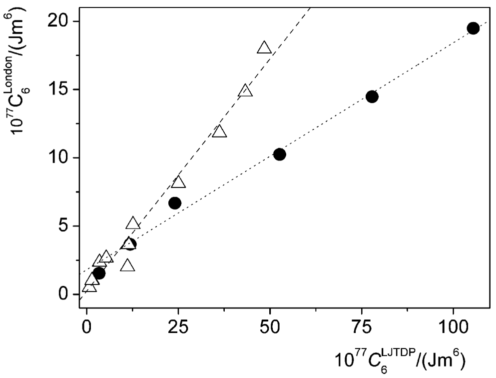

Figure 6. $C_6^{London} = 3\alpha^2I/4$ as a function of $C_6^{LJTDP} = n[R_m(T = 0\ K)]^6\epsilon(T = 0\ K)/(n\text{-}6)$ for, ●, the perfluoroalkanes CF_4, C_2F_6, C_3F_8, n-C_4F_{10}, n-C_5F_{12}, and n-C_6F_{14} and, △, the non-perfluoroalkanes Ar, CH_4, Kr, Xe, C_2H_6, SiF_4, SF_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, CCl_4, and $SiCl_4$. The compounds are listed by increasing value of C_6^{LJTDP}. The two symbols for CH_4 and Kr coincide. The dotted curve is the linear least-squares fit for the perfluoroalkanes and the dashed curve the corresponding fit for the non-perfluoroalkanes.

Table 4. Dimensionless Properties $B^* = B/(cm^3\cdot mol^{-1})$, $\eta^* = \eta/(\mu Pa\cdot s)$, and $\rho D^* = \rho D/(10^{-3}\cdot g\cdot m^{-1}\cdot s^{-1})$ of C_2F_6, C_3F_8, n-C_4F_{10}, n-C_5F_{12}, and n-C_6F_{14}

T	C_2F_6			C_3F_8			n-C_4F_{10}			n-C_5F_{12}			n-C_6F_{14}		
K	B^*	η^*	ρD^*	B^*	η^*	ρD^*	B^*	η^*	ρD^*	B^*	η^*	ρD^*	B^*	η^*	ρD^*
175	−855.5	9.075	11.67	−2320	8.544	11.00	−5596	7.561	9.707	−9518	7.180	9.172	−17680	7.138	9.113
180	−800.9	9.284	11.93	−2124	8.743	11.27	−4974	7.743	9.973	−8399	7.346	9.391	−15350	7.225	9.224
190	−707.2	9.699	12.47	−1803	9.140	11.80	−4011	8.121	10.52	−6683	7.676	9.825	−11860	7.521	9.608
200	−629.7	10.11	13.00	−1553	9.535	12.60	−3310	8.511	11.09	−5451	8.002	10.26	−9434	7.841	10.03
210	−564.6	10.52	13.52	−1353	9.930	13.13	−2784	8.894	11.65	−4536	8.325	10.69	−7686	8.157	10.44
220	−509.3	10.93	14.05	−1190	10.32	13.39	−2378	9.267	12.22	−3840	8.645	11.11	−6387	8.471	10.85
230	−461.7	11.33	14.57	−1056	10.72	13.92	−2058	9.660	12.81	−3297	8.96	11.54	−5401	8.782	11.26
240	−420.3	11.73	15.08	−943.2	11.12	14.45	−1801	10.09	13.44	−2865	9.279	11.96	−4633	9.090	11.67
260	−352.1	12.53	16.10	−765.5	11.91	15.51	−1415	11.10	14.78	−2227	9.907	12.80	−3530	9.698	12.47
280	−298.1	13.31	17.11	−632.1	12.71	16.56	−1141	12.05	16.18	−1784	10.53	13.64	−2789	10.30	13.27
300	−254.4	14.09	18.10	−528.5	13.51	17.61	−938.1	13.10	17.60	−1461	11.16	14.47	−2265	10.89	14.06
320	−218.3	14.85	19.07	−445.9	14.32	18.64	−782.2	14.18	19.04	−1216	11.79	15.30	−1878	11.49	14.84
340	−187.9	15.60	20.01	−378.4	15.12	19.67	−658.7	15.19	20.44	−1025	12.42	16.13	−1583	12.08	15.61
360	−162.1	16.34	20.92	−322.2	15.93	20.68	−558.6	16.31	21.86	−872.0	13.05	16.95	−1351	12.66	16.39
380	−139.8	17.07	21.80	−274.8	16.73	21.68	−475.8	17.50	23.31	−746.7	13.68	17.77	−1164	13.25	17.16
400	−120.5	17.78	22.68	−234.1	17.52	22.66	−406.2	18.38	24.56	−642.3	14.32	18.58	−1011	13.84	17.92
420	−103.4	18.50	23.56	−198.8	18.29	23.62	−346.7	19.37	25.86	−553.9	14.95	19.37	−883.2	14.42	18.68
440	−88.35	19.21	24.46	−167.9	19.06	24.55	−295.3	20.46	27.14	−478.1	15.58	20.15	−774.8	15.01	19.43
460	−74.90	19.91	25.35	−140.5	19.82	25.46	−250.5	21.27	28.18	−412.3	16.21	20.92	−681.9	15.59	20.18
480	−62.83	20.59	26.18	−116.1	20.56	26.35	−210.9	22.06	29.28	−354.5	16.82	21.68	−601.3	16.17	20.90
500	−51.94	21.25	26.96	−94.20	21.27	27.21	−175.7	22.88	30.39	−303.5	17.43	22.43	−530.7	16.75	21.62
550	−28.84	22.86	28.81	−47.94	22.98	29.25	−102.6	24.81	32.81	−198.0	18.91	24.18	−387.1	18.18	23.36
600	−10.25	24.44	30.74	−10.76	24.54	31.13	−45.01	26.31	34.89	−115.4	20.29	25.85	−277.0	19.56	25.08
650	5.03	25.96	32.62	19.96	25.97	32.86	1.76	27.77	36.90	−48.66	21.59	27.37	−189.7	20.89	26.63
700	17.82	27.39	34.30	45.93	27.26	34.43	40.67	29.02	38.60	6.80	22.78	28.76	−118.3	22.16	28.15
750	28.68	28.78	35.90	68.28	28.44	35.85	73.68	30.10	40.08	53.88	23.87	30.07	−58.72	23.36	29.59
800	38.03	30.14	37.48	87.83	29.50	37.16	102.2	30.98	41.24	94.57	24.86	31.25	−8.01	24.50	30.89
900	53.28	32.71	40.56	120.7	31.34	39.46	149.1	32.42	43.17	162.0	26.57	33.29	74.29	26.56	33.31
1000	65.16	35.14	43.50	147.7	32.86	41.37	186.5	33.42	44.49	216.5	27.98	35.02	138.9	28.36	35.45

Table 5. Coefficients for $R_m(T)$ According to Equation 6

molecule	$10^{10} A_1$ / m	B_1 / K	$10^{10} A_2$ / m	B_2 / K	$10^{14}\Delta R_m(T)^a$ / m
CF_4	0.1155 ± 0.0019	720.4 ± 4.2	0.25357 ± 0.00093	1749 ± 14	0.60
C_2F_6	0.0519 ± 0.0018	610.6 ± 7.1	0.11125 ± 0.00089	1502 ± 26	0.52
C_3F_8	0.735 ± 0.017	286.0 ± 4.9	2.378 ± 0.033	1451 ± 28	24
n-C_4F_{10}	1.610 ± 0.036	260.4 ± 4.6	4.979 ± 0.071	1425 ± 28	45
n-C_5F_{12}	0.952 ± 0.020	262.9 ± 4.5	2.870 ± 0.041	1427 ± 28	31
n-C_6F_{14}	0.737 ± 0.016	254.2 ± 4.4	2.175 ± 0.031	1415 ± 28	24

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

Table 6. Fit Parameters According to Equations 7 and 8 for the n-Perfluoroalkanes C_mF_{2m+2}, $m < 7^a$

property	fit parameter	CF_4	C_2F_6	C_3F_8	n-C_4F_{10}	n-C_5F_{12}	n-C_6F_{14}
B	P_1	97.43 ± 0.37	162.450 ± 0.055	364.4 ± 2.9	475.7 ± 1.9	626.9 ± 3.8	634.7 ± 2.5
	$10^{-4}P_2$	-4.767 ± 0.045	-8.9595 ± 0.0074	-21.90 ± 0.39	-27.47 ± 0.22	-39.55 ± 0.43	-46.21 ± 0.26
	$10^{-6}P_3$	-0.42 ± 0.16	-3.160 ± 0.011	13.4 ± 1.4	9.12 ± 0.67	19.1 ± 1.3	18.23 ± 0.79
	$10^{-9}P_4$	-0.559 ± 0.017	-0.4330 ± 0.0073	-4.13 ± 0.25	-4.286 ± 0.98	-7.97 ± 0.19	-11.51 ± 0.10
	P_5	0.0 (fixed)	40.42 ± 0.26	42.9 ± 1.4	74.63 ± 0.38	75.51 ± 0.39	84.32 ± 0.13
	$\Delta B/(cm^3 \cdot mol^{-1})$	0.31	0.017	0.93	0.92	1.8	1.3
η	P_1	1.017 ± 0.029	1.434 ± 0.034	3.056 ± 0.070	3.92 ± 0.72	2.66 ± 0.13	1.86 ± 0.11
	$10^{2}P_2$	6.091 ± 0.025	4.559 ± 0.032	2.253 ± 0.066	-0.71 ± 0.67	2.09 ± 0.12	2.95 ± 0.10
	$10^{5}P_3$	-1.709 ± 0.074	-1.004 ± 0.098	6.72 ± 0.20	20.1 ± 2.1	3.80 ± 0.38	0.38 ± 0.32
	$10^{8}P_4$	-0.890 ± 0.090	-0.57 ± 0.12	-9.81 ± 0.26	-28.0 ± 2.6	-4.96 ± 0.47	-0.55 ± 0.40
	$10^{11}P_5$	0.671 ± 0.038	0.386 ± 0.054	3.81 ± 0.11	11.6 ± 1.1	1.59 ± 0.21	-0.13 ± 0.17
	$10^{3}\Delta\eta/(\mu Pa \cdot s)$	8.3	7.2	15	154	28	23
ρD	P_1	0.872 ± 0.056	1.46 ± 0.14	2.41 ± 0.44	1.82 ± 0.79	2.417 ± 0.064	2.24 ± 0.10
	$10^{2}P_2$	8.518 ± 0.049	6.22 ± 0.13	4.39 ± 0.42	1.94 ± 0.74	3.416 ± 0.060	3.679 ± 0.097
	$10^{5}P_3$	-4.78 ± 0.14	-2.18 ± 0.41	4.6 ± 1.3	18.4 ± 2.3	3.63 ± 0.19	1.68 ± 0.30
	$10^{8}P_4$	1.62 ± 0.17	-0.41 ± 0.52	-8.6 ± 1.6	-27.6 ± 2.9	-6.08 ± 0.23	-3.11 ± 0.38
	$10^{11}P_5$	-0.140 ± 0.074	0.58 ± 0.23	3.59 ± 0.71	11.5 ± 1.2	2.29 ± 0.10	1.07 ± 0.17
	$10^{5}\Delta\rho D/(g \cdot m^{-1} \cdot s^{-1})$	1.6	3.0	9.5	17	1.4	2.2

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

perfluoroalkanes and, for comparison, the group consisting of Ar, Kr, Xe, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, CCl_4, $SiCl_4$, SF_6, and SiF_4. At this stage we want to stress only that within each group a systematic behavior is observed and that in view of the physically meaningful parameter C_6 the perfluoroalkanes behave as regularly as the alkanes C_mH_{2m+2}, which were extensively studied in our previous work.[13,14]

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 perfluoroalkanes. The results are given in Table 4.

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

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

The fitting constants A_1, A_2, B_1, and B_2 are given in Table 5. By using eq 3 they allow for a direct calculation of $\epsilon(T)$.

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

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

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

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

The so-obtained fit parameters are given in Table 6.

We note that our results present the first systematic study of the intermolecular interaction potential of the lower perfluorinated n-alkanes. It has become clear that due to a severe lack of experimental thermophysical and spectroscopic 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.

Acknowledgment

We are grateful to Dr. Geller for providing the results of ref 31.

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Received for review April 5, 2007. Accepted June 15, 2007. We thank the Deutsche Forschungsgemeinschaft for financial support.

JE700182N