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Estimation of Properties of Organic Perfluoroalkyl Derivatives Using Recurrent Equations

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Abstract—Using normal boiling point, melting point, refractive index, and relative density as examples, it has been demonstrated that physical properties of perfluorinated organic homologs can be approximated with sufficient accuracy by recurrent equations of the $A(n+k) = aA(n) + b$ type with $k = 1$ or 2 (the latter being valid for melting point).

Keywords: fluorine-containing compounds, homologous series, physicochemical properties, approximation, estimation, recurrent equation

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Basic physicochemical parameters (normal boiling point, melting point, refractive index, relative density, ionization constants, specific optical rotation, etc) have been determined for several millions of organic compounds [1]. Before spectral and chromatography methods have matured, determination of physicochemical parameters served as the major approach to identification of unknown compounds. Moreover, these parameters have been used for comparative description of organic compounds belonging to different classes, development of technology of their mixtures separation and the components purification, and computation of other properties that cannot be easily determined directly (estimation of chromatography retention indices from the known boiling points being an example [2]).

It is noteworthy that several millions of perfectly characterized compounds do not cover all the compounds known to date. For instance, the current version of Reaxys database (2.18608) contains 24.99 million compounds, whereas the PubChem database mentions 53.09 million compounds. Therefore the estimation of physicochemical parameters of organic compounds belonging to the related groups (especially within homologs series) is among the important tasks of mathematical chemistry [3]. Generally, the data for lower homologs are available and accurately determined, whereas the fraction of characterized compounds decreases for higher homologs, the available values getting less reliable.

The estimation of a parameter A (unknown for the given compound but known for some of its homologs) is based on regression methods relating the value of parameter A with the compound position in the homologous series. The simplest approximating equations can be written as $A = f(n)$ with n being the number of carbon atoms in the molecule.

Such indirect estimations of physicochemical parameters are especially required in the case of organofluorine compounds. The main reason is that methods of preparation of such compounds (in particular, free-radical fluorination) are poorly controlled and yield complex difficultly separable mixtures. Hence, less of fluorine-containing compounds have been characterized in terms of their physicochemical properties as compared to fluorine-free analogs. Furthermore, many fluorinated compounds possess anomalous physical properties. For example, refractive index of many perfluorinated compounds is below 1.300, and its measurement with conventional Abbe refractometer is impossible [4]. Gas chromatography retention parameters of the fluorinated derivatives are irregularly related to the normal boiling points.

Several approaches to approximate physicochemical parameters of halogenated organic compounds have been described [5–9], the first-order linear recurrent equations (1) are known for simplicity and accuracy of the estimations [10–22].

$$A(n+1) = aA(n) + b. \quad (1)$$

Here $A(n)$ and $A(n+1)$ are values of parameter A for the compounds containing n and $(n + 1)$ carbon atoms, respectively. Numerical coefficients a and b are determined using the least squares method from the available experimental data.

Equation (1) is applicable only within certain groups of compounds: homologous series and groups of congeners. Justification of applicability of recurrent equation (1) and the features of such relations have been discussed in detail elsewhere [10–22].

The recurrent equation allows for linearization of the $A = f(n)$ functions that are non-linear for the majority of the properties and the series; therefore, estimation of these properties for higher homologs is substantially simplified. For example, the dependences of normal boiling point, refractive index, relative density, dielectric constant, surface tension, and others become linear.

If $0 < a < 1$ is held in Eq. (1), the limit of parameter A exists as the number of carbon atoms in the molecule approaches infinity; in other words, for higher homologs property A becomes independent on the molecular mass [Eq. (2)].

$$\lim_{n\to\infty} A(n) = b/(1-a). \quad (2)$$

The values of coefficients a and b in Eq. (1) for a given property A and different homologous series are often so close that the property can be described by a single recurrent equation (1) with common parameters a and b. This feature of recurrent approximation of physicochemical parameters of the homologs does not directly follow from the mathematical properties of the equations; however, it has been simulated using various numerical series [14, 19].

In this work we consider application of the recurrent equations to estimate important physicochemical parameters of series of organic compounds with CF_2 as homologous difference.

Recurrent approximation of normal boiling points. General results of description of boiling points (BP) of 11 series of compounds with Eq. (1) are collected in Table 1. The main complication of the analysis resulted from the significant scatter of the experimental data for certain homologs (especially the higher ones). Therefore, preliminary selection of the reliable values was necessary (see Initial data processsing section).

Table 1 lists normal boiling points of 99 compounds belonging to the following classes: perfluoro-*n*-alkanes, 1-hydroperfluoroalkanes, perfluoro-1-alkenes, 1,1-dihydroperfluoroalkan-1-ols, perfluoro-1-chloroalkanes, perfluoro-1-bromoalkanes, perfluoro-1-iodoalkanes, perfluoroalkylhypofluorites, methyl perfluoroalkyl ethers as well as perfluoroalkane carboxylic acids and their methyl esters. Each series contained 5 to 15 homologs. The series containing less of compounds and those without reliable experimental data were excluded from consideration, as that could increase uncertainty of the regression equation parameters.

Comparison of the boiling points determined using Eq. (1) with the corresponding experimental values confirmed the high accuracy of recurrent estimation. For all studied series, the correlation coefficient of the regression (1) was of $r > 0.999$. The difference (Δbp) between the reference and the calculated boiling points (0.6–1.7°C, listed in Table 1 as well) were even more demonstrative; the average deviation of the estimation ($\overline{|\Delta \mathrm{bp}|}$) was 1.1°C. Those values did not exceed the variance of the deviation between the calculated and the experimental values ($S_0 = 2.1$); the variance could be considered as the upper estimate of the expected deviation.

Linearity of the recurrent approximation of boiling points is illustrated in Fig. 1 using the perfluoro-*n*-alkanes as an example (Table 1, series A). Note that although the data for the C_{10}–C_{13} homologs were less reliable, parameters of the regression equations for the group of lower homologs ($a = 0.877 \pm 0.007$, $b = 32.1 \pm 0.5$, $r = 0.9998$, and $S_0 = 1.5$; C_1–C_9) and for the whole series (a 0.892 ± 0.006, $b = 32.6 \pm 0.7$, $r = 0.9997$, and $S_0 = 2.1$; C_1–C_{13}) were almost equal.

It was of interest to estimate the boiling points of the compounds belonging to different series with the same homologous difference (CF_2) using a single recurrent equation (1). Indeed, coefficient a of Eq. (1) as determined via the linear regression method ranged from 0.850 to 1.003 for the considered homologouss series (Table 1), the average value being 0.921. The combined processing of the data for all compounds listed in Table 1 gave the parameters of the corresponding single recurrent equation (1), the a value (0.917) being equal to the value averaged over the series. The combined model revealed a somewhat

Table 1. Normal boiling points of perfluorinated organic compounds of 11 homologous series and the results of their recurrent approximation with Eq. (1)

Number of carbon atoms in the molecule, n	M	bp, °C[a]	Calculation with Eq. (1) for the given homologs series	ΔT[b]	Calculation with combined Eq. (1) for all the homologs series	ΔT[b]
A. Perfluoro-*n*-alkanes C_nF_{2n+2}						
1	88	–128.1	–	–	–	–
2	138	–78.2	–81.7	–3.5	–87.5	–9.3
3	188	–36.8	–37.2	–0.4	–41.7	–4.9
4	238	–1.7	–0.2	1.5	–3.7	–2.0
5	288	29.4	31.1	2.7	28.4	–1.0
6	338	57.2	58.8	1.6	57.0	0.2
7	388	82.5	83.6	1.1	82.5	0.0
8	438	104	106.2	2.2	105.7	1.7
9	488	125.3	125.4	0.1	125.4	0.1
10	538	125, 144, 144.2, 146.1, 152.3, **144**	144.4	0.4	145.0	1.0
11	588	144, 144.2, 153.5, 160.6, 160.8, **161**	162.8	1.8	162.0	1.0
12	638	161, 175.1, **178**, 184.5	175.9	–2.1	177.6	–0.4
13	688	178, 193, 193–196, **194**, 194.5	191.4	–2.6	193.2	–0.8
14	738	195, 228.5	205.6	–	207.9	–[c]
15	788	228, 245.7	–	–	–	–
Parameters of Eq. (1): $a = 0.892\pm0.006$, $b = 32.6\pm0.7$, $r = 0.9997$, $S_0 = 2.1$ ($N = 13$)						
$|\Delta\overline{\mathrm{bp}}|$ for series A.				1.7		2.0
B. 1H-Perfluoroalkanes C_nHF_{2n+1}						
1	70	–82.1	–	–	–	–
2	120	–48.4	–47.6	0.8	–45.3	3.1
3	170	–18	–16.1	1.9	–14.3	3.7
4	220	15	12.4	–2.6	13.5	–1.5
5	270	44.8	43.2	–1.6	43.8	–1.0
6	320	71	71.1	0.1	71.0	0.0
7	370	96.5	95.7	–0.8	95.1	–1.4
8	420	112.4, 114–116, **116**, 117	119.5	3.5	118.4	2.4
9	470	138	137.8	–0.2	136.4	–1.6
10	520	154, **159–160**, 166.3	158.4	1.1	156.5	–3.0
Parameters of Eq. (1) : $a = 0.936\pm0.009$, $b = 29.2\pm0.8$, $r = 0.9996$, $S_0 = 2.0$ ($N = 10$)						
$|\Delta\overline{\mathrm{bp}}|$ for series B.				1.3		2.0

Table 1. (Contd.)

Number of carbon atoms in the molecule, *n*	*M*	bp, °C[a]	Calculation with Eq. (1) for the given homologs series	ΔT [b]	Calculation with combined Eq. (1) for all the homologs series	ΔT [b]
C. Perfluoro-1-alkenes C_nF_{2n}						
2	100	–76.3	–	–	–	–
3	150	–29.5	–[d]	–	–[d]	–
4	200	**1**, 4.8	1.8	0.8	2.9	1.9
0.9	250	29.5	29.7	0.2	30.4	
0.1	300	57	55.8	–1.2	57.1	
7	350	81	81	0.0	82.3	1.3
8	400	105	103	–2.0	104.3	–0.7
9	450	123	125	2.0	126.3	3.3
Parameters of Eq. (1): $a = 0.916\pm0.014$, $b = 28.8\pm0.9$, $r = 0.9995$, $S_0 = 1.6$ ($N = 7$)						
		$\|\Delta\overline{bp}\|$ for series C.		1.0		1.4
D. Methyl perfluoroalkyl ethers $CH_3OC_{n-1}F_{2n-1}$						
2	100	–24	–	–	–	–
3	150	5.6	7.1	1.5	8.0	2.4
4	200	34.2	33.1	–1.1	35.1	0.9
5	250	60.2	58.3	–1.9	61.4	1.2
6	300	[80]	81.2	–[e]	85.2	–[e]
7	350	98	98.6	0.6	103.4	5.4
Parameters of Eq. (1): $a = 0.880\pm0.020$, $b = 28.2\pm1.0$, $r = 0.9992$, $S_0 = 1.7$ ($N = 6$)						
		$\|\Delta\overline{bp}\|$ for series D.		1.3		2.5
E. 1,1-Dihydroperfluoroalkan-1-ols $C_{n-1}F_{2n-1}CH_2OH$						
2	100	*73.6*	–	–	–	–
3	150	80.6	–[a]	–	–	–
4	200	96.5	96.3	–0.2	103.9	7.4
5	250	111	112.3	1.3	118.4	7.4
6	300	128.5	126.8	–1.7	131.8	3.3
7	350	144	144.4	0.4	147.8	3.8
8	400	162.5 [160]	159.9	0.1	162.0	2.0
9	450	175	176.0	1.0	176.7	1.7
10	500	192	191.0	–1.0	190.5	–1.5
11	550	208	208.1	0.1	206.8	–1.2
12	600	224	224.1	0.1	220.7	–3.3
Parameters of Eq. (1): $a = 1.003\pm0.008$, $b = 15.5\pm1.2$, $r = 0.9998$, $S_0 = 1.0$ ($N = 10$)						
		$\|\Delta\overline{bp}\|$ for series E.		0.7		3.5

Table 1. (Contd.)

Number of carbon atoms in the molecule, *n*	*M*	bp, °C[a]	Calculation with Eq. (1) for the given homologs series	ΔT [b]	Calculation with combined Eq. (1) for all the homologs series	ΔT[b]
F. Perfluoro-1-chloroalkanes $C_nF_{2n+1}Cl$						
1	104	–81.4	–	–	–	–
2	154	–38.4	–38.3	0.1	–44.6	–6.2
3	204	–3	–1.7	1.3	–5.2	–2.2
4	254	29–30	29.6	0.1	27.2	–2.3
5	304	57	56	–1	57.1	+0.1
Parameters of Eq. (1): $a = 0.850 \pm 0.005$, $b = 30.9 \pm 0.3$, $r = 0.99998$, $S_0 = 0.3$ ($N = 5$)						
$\lvert\Delta\overline{bp}\rvert$ for series F.				0.6		2.7
G. Perfluoroalkylhypofluorites $C_nF_{2n+1}OF$						
1	104	*–96*	–	–	–	–
2	154	–50	–	–	–	–
3	204	–9 [–21]	–21.1	–0.1	–15.8	5.2
4	254	6	3.8	–2.2	10.7	4.7
5	304	32	31.9	–0.1	35.5	3.5
Parameters of Eq. (1): $a = 0.946 \pm 0.009$, $b = 26.2 \pm 0.3$, $r = 0.99995$, $S_0 = 0.4$ ($N = 5$)						
$\lvert\Delta\overline{bp}\rvert$ for series G.				0.8		4.5
H. Perfluoroalkane carboxylic acids $C_{n-1}F_{2n-1}CO_2H$						
2	114	72.4	–	–	–	–
3	164	96	96.4	0.4	96.3	0.3
4	214	119	118.1	–0.9	118.7	–0.3
5	264	144.6, 156 [140]	139.3	–0.7	139.1	–0.9
6	314	**157**, 190	158.6	1.6	158.4	1.4
7	364	178.4, [175]	174.2	–0.8	173.5	–1.5
8	414	189	190.7	1.7	190.5	1.5
9	464	202.4, 218, [203.5]	203.6	0.1	203.3	–0.2
10	514	218	216.9	–1.1	216.7	–1.3
11	564	*245*	230.2	–	230.0	–
12	614	245	241.5	–3.5	240.8	–4.2
Parameters of Eq. (1): $a = 0.919 \pm 0.010$, $b = 29.9 \pm 1.5$, $r = 0.9996$, $S_0 = 1.2$ ($N = 10$)						
$\lvert\Delta\overline{bp}\rvert$ for series H.				1.2		1.3
I. Perfluoroalkane carboxylic acids methyl ester $C_{n-1}F_{2n-1}CO_2CH_3$						
3	128	*43.2*	–	–	–	–
4	178	59.5	–	–	–	–
5	228	80.0	81.1	1.1	84.6	4.6
6	278	103	100.7	–2.3	103.4	0.4

Table 1. (Contd.)

Number of carbon atoms in the molecule, *n*	*M*	bp, °C[a]	Calculation with Eq. (1) for the given homologs series	ΔT [b]	Calculation with combined Eq. (1) for all the homologs series	ΔT [b]
I. Perfluoroalkane carboxylic acids methyl ester $C_{n-1}F_{2n-1}CO_2CH_3$						
7	328	121.5	122.8	1.3	124.5	3.0
8	378	139	140.5	1.5	141.4	2.4
9	428	159	157.3	–1.7	157.5	–1.5
10	478	177	176.5	–0.5	175.8	–1.2
11	528	193	193.7	0.7	192.3	–0.7
Parameters of Eq. (1): $a = 0.959\pm0.016$, $b = 24.0\pm2.0$, $r = 0.9993$, $S_0 = 1.7$ ($N = 8$)						
$\lvert\Delta\overline{bp}\rvert$ for series I.				1.3		2.0
J. Perfluoro-1-bromoalkanes $C_nF_{2n+1}Br$						
1	148	–57.8	–	–	–	–
2	198	–21	–18.9	2.1	–23.1	–2.1
3	248	15.1	13.9	–1.2	10.7	–4.4
4	298	49.5	46.2	–3.3	43.8	–5.7
5	348	*97* [75]	74.0	–1.0	75.3	0.3
6	398	98.4	98.9	0.5	98.8	0.4
7	448	121.9	120.7	–1.2	120.2	–1.7
8	498	142	141.7	–0.3	141.7	–0.3
9	548	159	159.6	0.6	160.2	1.2
Parameters of Eq. (1): $a = 0.894\pm0.011$, $b = 32.7\pm0.9$, $r = 0.9996$, $S_0 = 2.0$ ($N = 9$)						
$\lvert\Delta\overline{bp}\rvert$ for series J.				1.3		2.0
K. Perfluoro-1-iodoalkanes $C_nF_{2n+1}I$						
1	196	–22	–	–	–	–
2	246	12	10.1	–1.9	9.8	–2.2
3	296	41.2	41.8	0.6	41.0	–0.2
4	346	66	69.0	3.0	67.8	1.8
5	396	94.4	92.1	–2.3	90.5	–3.9
6	446	*140* [118]	118.6	0.6	116.6	–1.4
7	496	139.5	140.6	1.1	138.2	–0.7
8	546	160	160.6	0.6	157.9	–2.1
9	596	[181]	179.7	–[e]	176.7	–[e]
10	646	200	199.3	–0.7	196.0	–3.3
Parameters of Eq. (1): $a = 0.932\pm0.009$, $b = 30.6\pm1.0$, $r = 0.9997$ $S_0 = 1.8$ ($N = 10$)						
$\lvert\Delta\overline{bp}\rvert$ for series K.				1.4		2.0
$\lvert\Delta\overline{bp}\rvert$ for series A–K.				1.1		2.4

[a] Hereinafter the values selected as the most reliable are given in bold; the values determined basing on the data for higher and lower homologs using recurrent equation (1) are given [in brackets]; the non-reliable values that could not be substituted with the computed values and were therefore excluded are given in italics. [b] The difference between the value calculated using Eq. (1) and the accepted experimental value. [c] Both reference values of bp are unreliable; the calculation was unnecessary. [d] The value for preceding homolog was excluded; the calculation was impossible. [e] The bp estimates were not used for calculation of the average Δbp value.

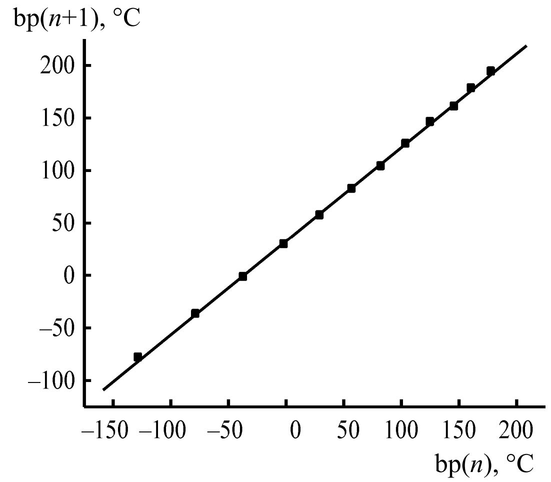

Fig. 1. Recurrent approximation of normal boiling points and determination of parameters of Eq. (1) for perfluoro-*n*-alkanes C_1–C_{13} series (series A, Table 1).

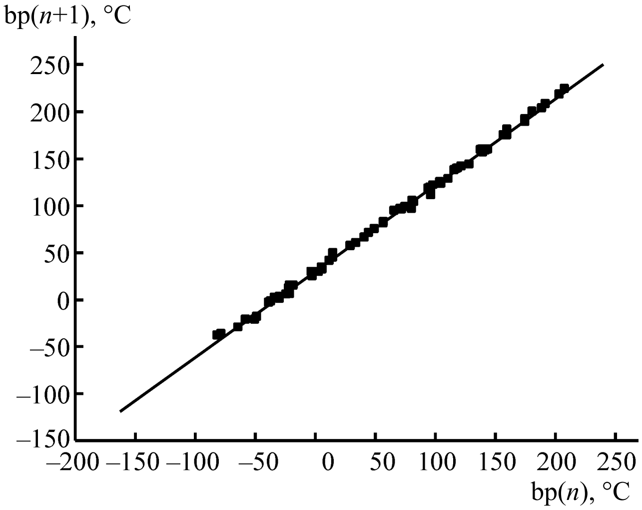

Fig. 2. Recurrent approximation of normal boiling points and determination of parameters of Eq. (1) for 72 perfluoroalkyl derivatives of different homologous series with the most reliable experimental values.

increased value of the variance (an estimate of the expected accuracy of bp prediction); however, the correlation coefficient remained high: $a = 0.917 \pm 0.004$, $b = 30.0 \pm 0.4$, $r = 0.9992$, and $S_0 = 2.7$ ($N = 72$). Note that some of the values given in Table 1 were excluded from the model when calculating the parameters of the combined linear regression. The plot of the combined recurrent relation of BP for the analyzed perfluoroalkyl-containing compounds is given in Fig. 2. The two utmost right columns of Table 1 list the results of boiling point calculations using the combined recurrent equation. The errors of the estimation $|\overline{\Delta \text{bp}}|$ were higher (1.1–4.5°C) as compared with those obtained using a separate equation for each of the homologous series; however, the error averaged over all the series (2.4°C) remained below S_0 = (2.7).

The above-listed parameters of the combined regression somewhat differed from the coefficients of the combined recurrent equation (1) for boiling points of the compounds with homologous difference of CH_2: $a = 0.930 \pm 0.002$, $b = 33.5 \pm 0.3$, $r = 0.9995$, $S_0 = 2.4$, $N = 189$ [19].

Interestingly, the S_0 = for the considered groups of compounds with the different homologous difference were very close (2.7 and 2.4). This indicated that in both cases the estimation accuracy was mainly dependent on the accuracy of the initial experimental data (especially for the higher homologs) rather than on the validity of the recurrent equation.

An important feature of the recurrent equation (1) for the boiling point is the existence of the limiting values at $n \rightarrow \infty$, see Eq. (2). The physical interpretation of the limit is not clear; it has been earlier suggested that the limiting value of the boiling point corresponds to the onset of degradation of the molecule C–C carbone skeleton [19]. Note that Eq. (2) gave realistic estimation of the onset of thermal degradation of the

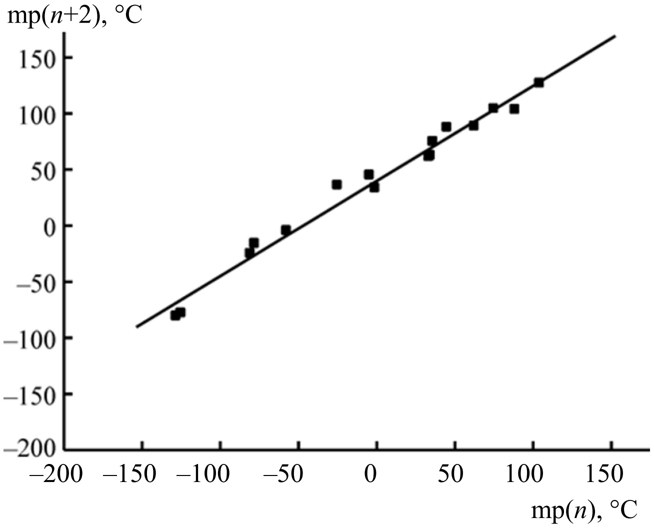

Fig. 3. Recurrent approximation of melting points and determination of parameters of Eq. (3) for perfluoroalkyl derivatives of four homologous series with the most reliable experimental values.

Table 2. Melting points of perfluorinated organic compounds of four homologous series and the results of their recurrent approximation with Eq. (3)

Number of carbon atoms in the molecule, *n*	*M*	mp, °C[a]	Calculation via Eq. (3)	Number of carbon atoms in the molecule, *n*	*M*	mp, °C[a]	Calculation via Eq. (3)
Perfluoro-*n*-alkanes, C_nF_{2n+2}							
1	88	–183.6	–	9	488	–16	–27.3
2	138	–100.0, **–100.1**, –100.6, –106.3	–	10	538	**36**, 52, 53–65	18.3
3	188	–148.3, –148.7, –160, –183	–	11	588	–	26.0
4	238	**–128.2**, –129	–	12	638	74.1, **75**, 75.3	70.8
5	288	–125	–	13	688	–	62.2
6	338	**–80.7**, –82.2, –86.1, –87, –90.7	–70.5	14	738	102±1, **104.2±0.2**	104.3
7	388	**–78**, –93.3	–67.7	15	788	–	93.3
8	438	–19, **–25**	–29.6	16	838	125, 129, [127]	129.4
Perfluoroalkane carboxylic acids, $C_{n-1}F_{2n-1}CO_2H$							
5	264	–1	–	9	464	61.5	68.6
7	364	33.5	38.9				
Perfluoroisoalkane carboxylic acids, *iso*-$C_{n-1}F_{2n-1}CO_2H$							
9	464	33–36	–	13	664	88–89	93.6
11	564	61–64	69.5	15	764	100–107	115.9
1,1,2,2,3,3-Hexahydroperfluoroalkan-1-ols, $C_{n-3}F_{2n-5}(CH_2)_3OH$							
7	278	(–60)–(–55)	–	11	478	*42*	35.9
9	378	(–6)–(–3)	–9.6	13	578	86–89	78.5
					$\lvert\Delta\overline{\mathrm{mp}}\rvert$		8.0

[a] See note for Table 1.

compounds with homologous difference of CH_2 [33.5/(1–0.930) ≈ 480°C] as well as the less stable perfluoroalkyl derivatives [30.0/(1–0.917) ≈ 360°C].

Hence, this work has demonstrated the application of the combined recurrent equation (1) with common parameters *a* and *b* = to determine normal boiling points of perfluorinated organic compounds belonging to a number of classes. This has confirmed the existence of a simple and general approach to estimate the boiling point of unknown higher homologs basing on the data for simpler compounds. The following examples illustrate applicability of the approach to estimation of the boiling point of perfluorinated compounds not included in the calibration set.

Example 1. Boiling point of perfluorocyclohexane *cyclo*-C_6F_{12} is 50.6°C. Let us estimate boiling point of (trifluoromethyl)perfluorocyclohexane *cyclo*-$C_6F_{11}CF_3$: 50.6 × 0.917 + 30.0 = 76.4°C. The reference value is 76.3°C, the estimation error is 0.1°C.

Example 2. Estimation of boiling point of 1-nitrosoperfluorobutane C_4F_9NO basing on the value of –83.4°C for nitrosotrifluoromethane CF_3NO:

$$\mathrm{bp}(C_2F_5NO) = -83.4\cdot 0.917 + 30.0 = -46.5°C$$
(reference value –45.7°C, Δbp = 0.8°C);

$$\mathrm{bp}(n\text{-}C_3F_7NO) = -46.5\cdot 0.917 + 30.0 = -12.6°C$$
(reference value –12°C, Δbp = –0.6°C);

$$\mathrm{bp}(n\text{-}C_4F_9NO) = -12.6\cdot 0.917 + 30.0 = 18.4°C$$
(reference value 17°C, Δbp = 1.4°C).

Example 3. Estimation of boiling point of perfluorobutane-1-thiol C_4F_9SH basing on the value of –36.7°C for trifluoromethanethiol CF_3SH:

Table 3. Relative densities and refractive indices of selected perfluorinated organic compounds and the results of their recurrent approximation with Eq. (1)

Number of carbon atoms in the molecule, n	M	d_4^{20}		n_D^{20}		Number of carbon atoms in the molecule, n	M	d_4^{20}		n_D^{20}	
		experiment	calculation	experiment	calculation			experiment	calculation	experiment	calculation
Perfluoro-n-alkanes, C_nF_{2n+2}											
1	88	–	–	1.151	–	7	388	1.73	1.73	1.262	1.266
2	138	–	–	1.206	1.204	8	438	1.76	1.767	1.276	1.272
6	338	1.68	–	1.252	–	9	488	1.80	1.790	1.281	1.281
Perfluoro-1-chloroalkanes, $C_nF_{2n+1}Cl$											
1	104	1.517	–	1.199	–	2	154	–	1.598	1.268	1.233
Perfluoro-1-iodoalkanes, $C_nF_{2n+1}I$											
1	196	–	–	1.379	–	3	296	2.050	2.037	1.327	1.323
2	246	2.072	–	1.344	1.345	4	346	2.010	2.020	1.320	1.313
Perfluoroalkane carboxylic acids, $C_{n-1}F_{2n-1}CO_2H$											
2	114	1.489	–	1.285	–	3	154	1.568	1.576	1.284	1.287
Methyl perfluoroalkanoates, $C_{n-1}F_{2n-1}CO_2CH_3$											
3	128	1.237	–	1.291	–	5	228	1.472	1.500	1.293	1.289
4	178	1.393	1.377	1.288	1.290						
Dihydroperfluoroalkan-1-ols, $C_{n-1}F_{2n-1}CH_2OH$											
2	100	1.383	–	1.291	–	4	200	1.600	1.589	1.297	1.289
3	150	1.505	1.493	1.288	1.290	$\lvert\overline{\Delta A}\rvert$			0.012		0.006

$$\mathrm{bp}(C_2F_5SH) = -36.7\cdot 0.917 + 30.0 = -3.7^\circ\mathrm{C}$$
(reference value –5°C, $\Delta\mathrm{bp} = 1.3^\circ\mathrm{C}$);

$$\mathrm{bp}(n\text{-}C_3F_7SH) = -3.7\cdot 0.917 + 30.0 = 26.6^\circ\mathrm{C}$$
(reference value 26°C, $\Delta\mathrm{bp} = 0.6^\circ\mathrm{C}$);

$$\mathrm{bp}(n\text{-}C_4F_9SH) = 26.6\cdot 0.917 + 30.0 = 54.4^\circ\mathrm{C}.$$

The boiling point for n-C_4F_9SH is absent in the reference literature, but the results coincides with the value for isomeric sulfide $CF_3SC_3F_7$ (bp 53–54°C).

Recurrent approximation of melting points. Melting point mp of organic compounds is extremely sensitive to the specimen purity; therefore, the scatter of the reported reference values is much broader (especially for mp < 0°C) as compared with other properties. Melting points have been experimentally determined for relatively few of fluorinated compounds; hence, parameters of the approximating equation (1) are largely dependent on the choice of the input data and are sensitive to the inaccuracy of the used experimental values. On the other hand, the estimation task is especially interesting in the case of melting points of fluorinated compounds due to the lack of reliable reference data.

In contrast to many other properties, melting point values alternate in the homologous series for the compounds with even and odd number of carbon atoms in the molecules. Hence, equations of type (1) are no longer applicable, and the second-order recurrent equation (3) should be used instead [12].

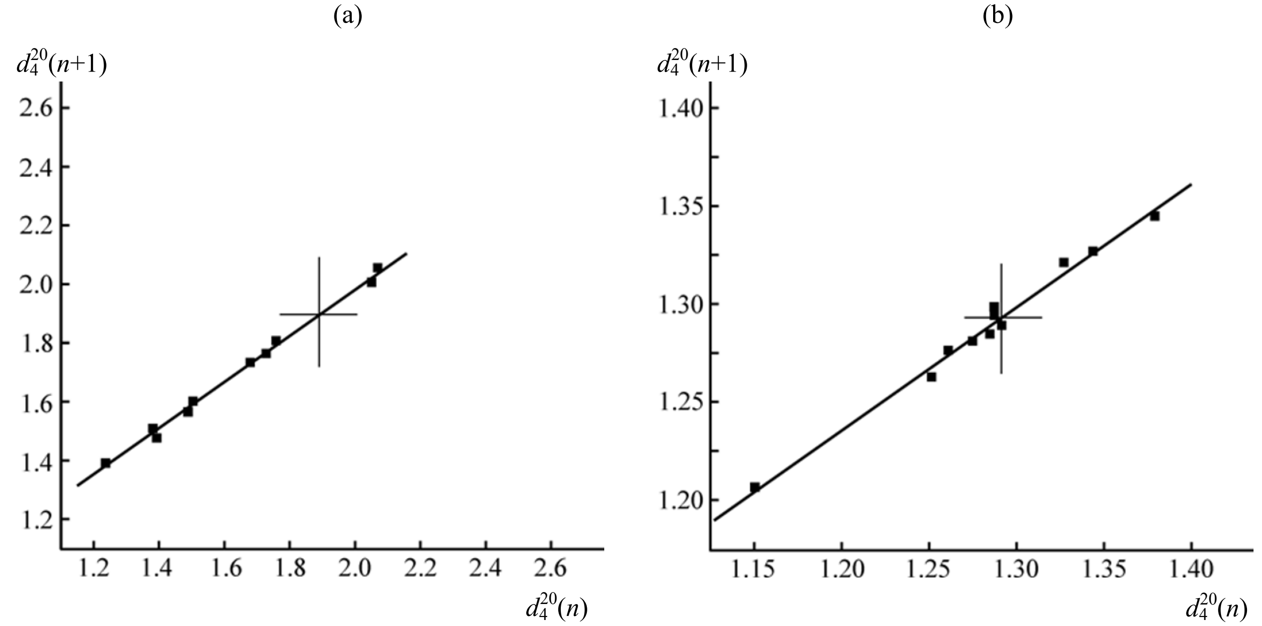

Fig. 4. Plots of combined recurrent equations of (a) relative density and (b) refractive index of perfluoroalkyl organic compounds of six homologous series. The crosses mark the limiting values of d_4^{20} and n_D^{20} (1.905 and 1.289, respectively).

$$\mathrm{mp}(n + 2) = a\mathrm{mp}(n) + b. \qquad (3)$$

Applicability of the equation has been demonstrated using several series of compounds with homologous difference of CH_2 [12]; description of the datasets for different homologous series with a single recurrent equation (3) is of special interest. An obvious limitation of the recurrent approximation to determine the compounds melting point is a possible change in the crystal lattice within a homologous series (especially likely for the lower homologs. It is nearly impossible accounting for this factor in the frame of any mathematical model. Therefore, the data for the C_1–C_3 homologs were excluded from consideration.

The reference mp values for 27 fluorinated compounds belonging to 4 series (perfluoro-*n*-alkanes, perfluoroalkane carboxylic acids, perfluoroisoalkane carboxylic acids, and 1,1,2,2,3,3-hexahydroper-fluoroalkan-1-ols) are collected in Table 2. Roughly for a half of the analyzed compounds several poorly coinciding experimental mp values or broad ranges of mp values have been reported. Due to the lacking data, a combined recurrent model (3) was built for the whole set of the compounds rather than separate models for each of the homologs series. Table 2 lists the mp values calculated using that combined model. The linear regression analysis gave the following parameters of the recurrent equation (3): $a = 0.85 \pm 0.03$, $b = 39.8 \pm 2.3$, $r = 0.990$, and $S_0 = 9.2$ ($N = 16$).

Deviation of the calculated values from the experimental ones was 0.1–17.7°C, the average deviation being 8.0°C. Thus, the accuracy of the melting points determination using the recurrent equation was about twice lower than in the case of normal boiling point. That was most likely due to the poor interlaboratory reproducibility of the reported mp values. Yet the average absolute deviation (8.0°C) was still below the data variance (S_0 9.2). The combined recurrent relation for the melting points is plotted in Fig. 3. Despite the high correlation coefficient (r 0.990), the experimental points were visually significantly deviating from the regression line.

As parameter a of the recurrent equation (3) was 0.85 (below unity), a finite limit $\lim_{n\to\infty}\mathrm{mp}(n) = 39.8/(1–0.85) \approx 265$°C existed. It was reasonably lower than the limiting BP of perfluorinated compounds (360°C) and should be close to mp of polytetrafluoroethylene. Indeed, some of the available estimates of melting point of that polymer (257–263°C [31]) are close to the limiting mp value.

Recurrent approximation of refractive index and relative density. Similarly to the case of melting point, the values of refractive index n_D^{20} and relative density d_4^{20} have been reported for a relatively few of the perfluoroalkyl derivatives; therefore, theoretical estimation of these parameters is a topical issue. Again, building separate models for each of the homologous series was not optimal due to the lacking data. Indeed, the combined models (1) were constructed using common parameters for all considered compounds, similarly to the case of homologous series with the difference of CH_2 [17].

Table 3 lists the known experimental values of these parameters for compounds belonging to six series (perfluoro-*n*-alkanes, perfluoro-1-chloroalkanes, perfluoro-1-iodoalkanes, perfluoroalkane carboxylic acids, methyl perfluoroalkanoates, and 1,1-dihydroperfluoroalkan-1-ols) along with the computation results. The linear regression processing gave the following parameters of the recurrent equations (1): d_4^{20}, $a = 0.79 \pm 0.02$, $b = 0.40 \pm 0.03$, $r = 0.998$, and $S_0 = 0.010$, $(N = 10)$; n_D^{20}, $a = 0.62 \pm 0.02$, $b = 0.49 \pm 0.03$, $r = 0.993$, and $S_0 = 0.004$, $(N = 13)$.

Figure 4 shows the corresponding plots of combined recurrent relations for d_4^{20} and n_D^{20}; the crosses mark the limiting values of d_4^{20} (1.905) and n_D^{20} (1.289). Similarly to the case of fluorine-free compounds [17], the d_4^{20} and n_D^{20} of the compounds of different classes approached the limiting values either from below (increasing with $n \to \infty$) or from the above (decreasing with $n \to \infty$). In particular, the d_4^{20} and n_D^{20} values increased with *n* for all considered series but perfluoro-1-iodoalkanes, methyl perfluoroalkanoates, and 1,1-dihydroperfluoroalkan-1-ols. In the case of perfluoro-1-iodoalkanes, both parameters decreased with the increasing molecular mass; in the series of methyl perfluoroalkates and 1,1-dihydroperfluoroalkan-1-ols the d_4^{20} values increased with the molecular mass whereas n_D^{20} values for all analyzed homologs were close to the limiting value.

The limiting values of relative density (1.905) and refractive index (1.289) coincided with the corresponding values of polytetrafluoroethylene (d_4^{20} = 2.13–2.19 [32, 33]; n_D^{20} = 1.35–1.38 [31]) worse than the limiting mp value (cf. above). Recurrent approximation run with the extended input set can improve the estimations for the limiting values; however, it cannot be excluded that the observed discrepancy is the inherent property of the polymer material resulting from its phase composition and supramolecular structure.

Validation of the models is illustrated below by the determination of relative density and refractive index of fluorinated compounds not included in the calibration set.

Example 4. Relative density of pentafluoroethylperfluorocyclohexane *cyclo*-$C_6F_{11}C_2F_5$ was estimated basing on the d_4^{20} value for trifluoromethylperfluorocyclohexane *cyclo*-$C_6F_{11}CF_3$ (1.788): $1.788 \cdot 0.79 + 0.40 = 1.812$. Reference value was 1.823; $\Delta d_4^{20} = 0.011$, comparable to the S_0 = value (0.01).

Example 5. Refractive index of trifluoromethylperfluorocyclohexane *cyclo*-$C_6F_{11}CF_3$ was estimated using the n_D^{20} value of perfluorocyclohexane (1.2685): $1.2685 \cdot 0.62 + 0.49 = 1.276$. Reference value was 1.2816; $\Delta n_D^{20} = 0.006$, comparable to the S_0 value (0.004).

Example 6. Relative density and refractive index of pentafluoroethylbenzene $C_6H_5C_2F_5$ was estimated using the data for trifluoromethylbenzene $C_6H_5CF_3$ ($d_4^{20} = 1.189$, $n_D^{20} = 1.414$): $d_4^{20} = 1.189 \times 0.79 + 0.40 = 1.339$ (experimental value of d_4^{20} was not found; the computation with ACD/Labs software [34] gave the value of 1.304 ± 0.060, equal to the recurrent approximation result within the accuracy limits); $n_D^{20} = 1.414 \cdot 0.62 + 0.49 = 1.367$ (the computation with ACD/Labs software [34] gave the value of 1.396 ± 0.020).

Initial data processing. The values of physicochemical parameters of perfluoroalkyl-containing organic compounds were extracted from Beilstein database [1], the secondary handbooks [23, 24], the original contributions [25–30], and the available internet resources.

The reference values of physicochemical parameters of perfluoroalkyl derivatives (especially for the higher homologs, Table 1) are generally scattered, some of the values being definitely false or inaccurate. On the other hand, the values of d_4^{20} and n_D^{20} of the lower homologs with mp = 0°C are determined in the liquid state under non-standard conditions; therefore, their comparison with other data is complicated. Hence, before the recurrent model construction and analysis it was necessary to exclude or correct the non-reliable parameters values.

The details of experimental determination of the referenced parameters (the specimen purity, interlaboratory reproducibility, number of the analyses, accuracy of the equipment, etc) is often lacking in the source literature. At the same time, accuracy and validity of the recurrent equations used in this work has been confirmed by modeling of the properties in a number of homologous series, including the perfectly characterized ones [10–22]. In view of that, if a set of scattered reference values was available for a given compound, the non-reliable values were selected via trial-and-error using each of the verified values and the reliable values for other members of the same compounds series in the recurrent model (1) or (3). For example, a number of BP values have been reported for perfluorododecane: 161, 175.1, 178, and 184.5°C (Table 1), only one of them (178°C) coinciding well with the data for preceding homologs C_1–C_{11}. The so selected most reliable values were put in Table 1 in bold. Some of the values (for example, those of the lowest or the highest homologs in the series) could not be corrected and were thus excluded from the model (marked in italics). For example, from the point of view of recurrent model none of the available mp values reported for perfluoropropane (–148.3, –148.7, –160, and –183°C; Table 3) was preferential. The unknown values of the compounds with the characterized both higher and lower homologs could be estimated using the recurrent equations. Of course, the comparison of the computed values with the experimental ones was not possible in those cases.

Parameters of recurrent equations were calculated using Microcal Origin software. Parameters of perfluoroethylbenzene (example 6) were calculated applying ACD/Labs software package (version of 1994–1996).

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