Sorption characteristics of polyfluorocarboxamides

V. E. Kirichenko, E. P. Promyshlennikova, and K. I. Pashkevich*

Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,
20 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation.
Fax: +7 (343 2) 44 4133

The dependence of the variations in the differential molar free energy of sorption of polyfluorocarboxamides $R_FC(O)NR_2$ ($R_F = CF_3(CF_2)_i$, $i = 0$ to 5, R = H or Me) on capillary columns on the molecular structure of the amides, the temperature of analysis, and the nature of the stationary phases (OV-101, XE-60, and PEG-40M) were investigated by GLC. The peculiarities of the variation of the sorption characteristics of amides in XE-60 and PEG-40M polar phases, which cause the inversion of the order of retention of the members of pseudohomologous series, were found.

Key words: gas-liquid chromatography; polyfluorocarboxamides, sorption energy.

The relationship of the thermodynamic parameters of sorption of compounds to their structure and the properties of sorbents during chromatography are of substantial interest for understanding the character of the interaction of a substance with a stationary phase (SP).[1]

We have previously studied the variation in the parameters of sorption of a homologous series of esters of saturated perfluorocarboxylic acids (PFA) on various stationary phases[2] and have shown that a carboxylic and a perfluoroalkyl group present in the same molecule exert a complex effect on the mechanism of the retention of the compound when it is subjected to chromatography. To elucidate the effect of the amide functional group on the retention of derivatives of fluoro-containing acids, we have studied the gas-chromatographic behavior of 12 amides of PFA on glass capillary columns with OV-101, XE-60, and PEG-40M phases and calculated their retention indices.[3]

In the present work, we have studied features of the variation of the contributions of difluoromethylene units to the differential molar free energy of sorption, $-\Delta G_i(CF_2)$, for 12 amides of saturated perfluorinated carboxylic acids of the general formula $C_nF_{2n+1}C(O)NR_2$ ($n = 1$ to 6, R = H, Me). We regarded these compounds as two homologous series: amides $CF_3(CF_2)_iC(O)NH_2$ ($i = 1$ to 5) and dimethylamides $CF_3(CF_2)_iC(O)NMe_2$ ($i = 1$ to 5).

Experimental

Amides and dimethylamides of perfluorocarboxylic acids (APFA and DMA PFA, respectively) were analyzed on a Biokhrom-1 gas chromatograph with a flame ionization micro detector and glass capillary columns (50 m×0.25 mm). OV-1 (polydimethylsiloxane), XE-60 (cyanoethylsiloxane), and PEG-40M (polyethyleneglycol) were used as SP. The temperature range of the investigations was 60—130 °C for APFA and 60—100 °C for DMA PFA; the conditions of the measurements were isothermal. The separation of the amides of each of the homologous series was carried out at 4—5 temperatures at intervals of 10 °C. The experimental conditions have been described in more detail previously.[3]

The energetic contribution of one difluoromethylene unit was calculated from the corrected retention times (t') of the neighboring homologs:

$$\Delta G_i(CF_2) = -RT_a\ln(t'_i/t'_{i-1}), \qquad (1)$$

where i is the number of a difluoromethylene unit ($i = 1$ to 5); R is the universal gas constant; T_a/K is the temperature of the analysis.

The error in the determination of $\Delta G_i(CF_2)$ did not exceed 0.01 kJ mol^{-1}.

Results and Discussion

We considered the features of the variation in the sorption energy of APFA and DMA PFA as the length of the carbon chain varied, for three types of stationary phases: a nonpolar dimethylsiloxane phase (OV-101), a phase of medium polarity containing polar nitrile groups (XE-60), and a polar phase containing no functional groups (PEG-40M). This allowed us to reveal the role of nonspecific interactions between the sorbent and the sorbate. The formal parameter $-\Delta G_i(CF_2)$, the contribution of a CF_2 unit to the differential molar free energy of sorption (Tables 1, 2), was used in the discussion of the sorption processes.

The results obtained (Figs. 1 and 2; see Tables 1, 2) indicate that the character of the interaction of the first four members of the APFA and DMA PFA pseudohomologous series with a stationary phase depends to a great extent on the nature of the stationary phase. When

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Table 1. The values of the energy of sorption of difluoromethylene units, $-\Delta G_i(CF_2)$/J mol^{-1}, in the pseudohomologous series of perfluorocarboxamides $CF_3(CF_2)_iC(O)NH_2$

i	OV-101		
	80 °C	90 °C	100 °C
1	517.1	451.1	408.0
2	1115.3	1055.8	1000.2
3	1223.2	1147.3	1084.2
4	1264.7	1193.9	1124.2
5	1283.4	1212.3	1150.2
i	XE-60		
	100 °C	110 °C	120 °C
1	−217.1	−276.6	−338.4
2	645.1	590.3	556.2
3	677.5	620.0	586.5
4	683.3	624.0	588.4
5	686.6	627.4	591.2

the number of CF_2 groups $i \geq 3$, the energy of sorption of a molecule on any of the SP increases practically monotonically.

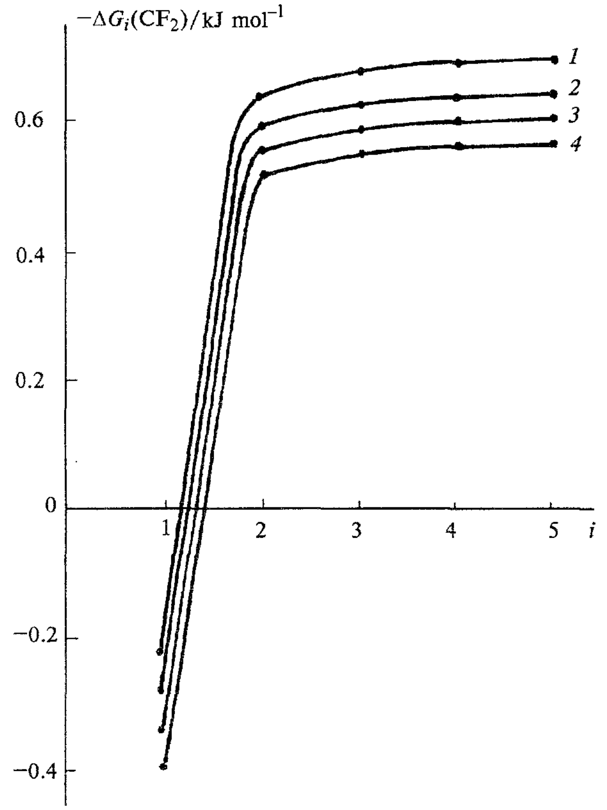

Fig. 1. The dependence of the differential molar free energy of sorption of a difluoromethylene unit, $-\Delta G_i(CF_2)$, on the number of the unit (*i*) in the APFA series, $CF_3(CF_2)_iC(O)NH_2$, on XE-60 at T_a = 100 °C (*1*), 110 °C (*2*), 120 °C (*3*), and 130 °C (*4*).

Table 2. The values of the energy of sorption of difluoromethylene units, $-\Delta G_i(CF_2)$/J mol^{-1}, in the pseudohomologous series of the dimethylamides of perfluorocarboxylic acids, $CF_3(CF_2)_iC(O)NMe_2$

i	OV-101		
	60 °C	70 °C	80 °C
1	670.6	628.2	595.7
2	1009.2	952.5	907.2
3	1211.5	1155.9	1120.5
4	1277.4	1224.6	1191.5
5	1283.6	1235.2	1199.9
i	XE-60		
	80 °C	90 °C	100 °C
1	−323.7	−363.6	−402.0
2	366.9	327.1	289.2
3	545.7	498.9	453.1
4	681.2	637.8	590.6
5	735.8	690.8	645.3
i	PEG-40M		
	60 °C	70 °C	80 °C
1	−616.2	−652.2	−713.2
2	216.4	97.1	−7.7
3	844.9	706.6	606.5
4	1298.3	1157.0	1067.9
5	1448.7	1327.8	1266.7

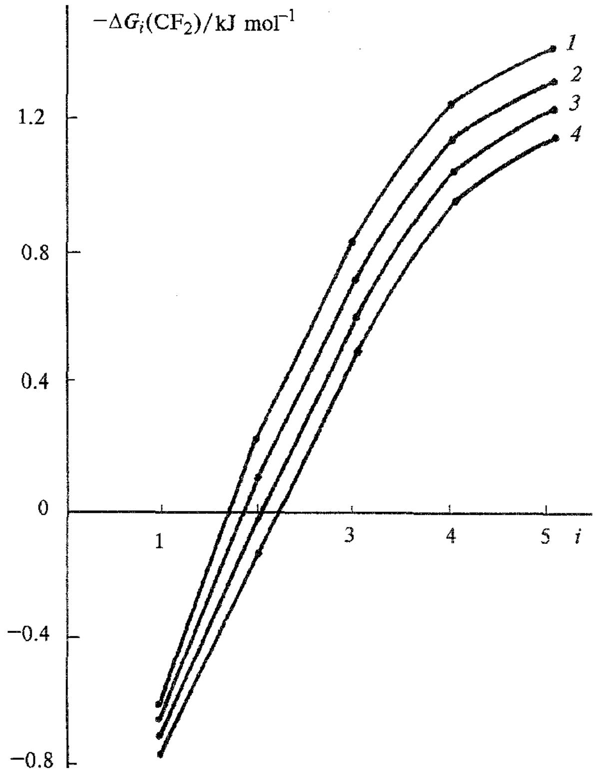

Fig. 2. The dependence of the differential molar free energy of sorption of a difluoromethylene unit, $-\Delta G_i(CF_2)$, on the number of the unit (*i*) in the DMA PFA series, $CF_3(CF_2)_iC(O)NMe_2$, on PEG-40M at T_a = 60 °C (*1*), 70 °C (*2*), 80 °C (*3*), and 90 °C (*4*).

In the sorption of APFA and DMA PFA on OV-101, $\Delta G_1(CF_2)$ is smaller than the other contributions. The $\Delta G_i(CF_2)$ values for APFA are somewhat greater than those for the corresponding DMA PFA, except for $\Delta G_1(CF_2)$. At the same time, at $i > 1$ the $\Delta G_i(CF_2)$ contributions are close to the corresponding values for the pseudohomologous series of ethyl and methyl perfluorocarboxylates (EPFA) that we studied previously.[2] As the first difluoromethylene unit is introduced, the $\Delta G_i(CF_2)$ contribution to the energy of sorption varies in the series: $\Delta G_1(CF_2)_{APFA} < \Delta G_1(CF_2)_{DMA\ PFA} < \Delta G_1(CF_2)_{EPFA}$. For subsequent i ($1 < i < 5$) the $\Delta G_i(CF_2)_{DMA\ PFA} < \Delta G_i(CF_2)_{APFA} < \Delta G_i(CF_2)_{EPFA}$ relationship holds.

Based on the analogous character of the interaction of perfluoromethylene fragments in APFA, DMA PFA, and EPFA at $i > 4$, we calculated the increase in the energy of sorption on going from an ester group to the corresponding amide group from Eqs. (2) and (3), by comparing compounds with close molecular weights: $C_6F_{13}C(O)NH_2$ (**1**) — $C_6F_{13}C(O)OMe$ (**2**) and $C_6F_{13}C(O)NMe_2$ (**3**) — $C_6F_{13}C(O)OEt$ (**4**).

$$\Delta G_{i(1)} - \Delta G_{i(2)} = - RT_a \ln[t'_{(1)}/t'_{(2)}], \quad (2)$$

$$\Delta G_{i(3)} - \Delta G_{i(4)} = - RT_a \ln[t'_{(3)}/t'_{(4)}], \quad (3)$$

where $t'_{(1)}$, $t'_{(2)}$, $t'_{(3)}$, and $t'_{(4)}$ are the corrected retention times of compounds **1**—**4**, respectively. The increase in $\Delta G_i(CF_2)$ on OV-101 at 100 °C was 5.4 kJ mol^{-1} for an amide group and 4.1 kJ mol^{-1} for a dimethylamide group. This implies that the energy of the formation of hydrogen bonds between APFA and the SF contributes to the energy of sorption of the amides of PFA.

The fact that $\Delta G_i(CF_2)$ for compounds **1** and **3** is higher than that of methyl and ethyl perfluoroheptanoates points to the fact that amides interact with the stationary phase more strongly than esters.

The $\Delta G_i(CF_2)$ values for the XE-60 phase are lower than those for OV-101 for both APFA and DMA PFA, as was determined previously[2] for esters of PFA. A distinction from EPFA is that the energy of sorption of a molecule substantially decreases on going from trifluoroacetates to pentafluoropropionates, *i.e.*, the $\Delta G_1(CF_2)$ value for the introduction of the first CF_2 unit is opposite in sign to the other contributions. When subsequent CF_2 units are introduced into a molecule of DMA PFA, $\Delta G_i(CF_2)$ increases monotonically up to $i = 5$, while in the case of APFA, the values of $\Delta G_i(CF_2)$ are nearly equal at $i \geq 3$.

The fact that the energy of sorption of $C_2F_5C(O)NR_2$ on XE-60 is lower than that of $CF_3C(O)NR_2$ results in the inversion of the order of retention of the lower pseudohomologs ($i = 1$ to 3). Then, on going to $C_3F_7C(O)NR_2$, the energy of sorption is greater than that of $C_2F_5C(O)NR_2$, but it may be either smaller or greater than the energy of sorption of $CF_3C(O)NR_2$ or may be equal to it. From the dependence of $\Delta G_i(CF_2)$ on i shown in Fig. 2 the tendency toward the inversion in the retention time for APFA can be seen. Taking into account the temperature dependence of $\Delta G_i(CF_2)$ (see Tables 1, 2) one may conclude that the retention of unsubstituted amides of PFA under optimal analysis conditions ($T_a \leq 140$ °C) varies in the order: $C_2F_5 < CF_3 < C_3F_7 < C_4F_9 < C_5F_{11} < C_6F_{13}$.

Under optimal conditions of separation ($T_a \leq 130$ °C), dimethylamides of PFA emerge from the column in the following order: $C_2F_5 < C_3F_7 \lesssim CF_3 < C_4F_9 < C_5F_{11} < C_6F_{13}$.

The homologs with $i \geq 4$ CF_2 groups are not involved in the processes of retention inversion. The $\Delta G_i(CF_2)$ contributions at $i \geq 4$ are close to the corresponding $\Delta G_i(CF_2)$ values for PFA esters.[2] The inversion in the retention of amides of PFA on XE-60 is much more pronounced than in the case of PFA esters, since the greatest changes in the retention order of PFA esters have only been observed for compounds having long alkyl chains.

The increase in the energy of sorption of compound **1** with respect to **2** and that of compound **3** with respect to **4** on XE-60 at 100 °C amounted to 12.7 and 6.7 kJ mol^{-1}, respectively. This indicates as well that the interaction of amides with the SP is greater than that of PFA esters.

The polar PEG-40M polyether phase turned out to be unsuitable for efficient separation of members of the homologous series of unsubstituted APFA due to the combination of great and similar retention times and poor separation of neighboring peaks. Therefore, the results are only presented for DMA PFA (see Table 2, Fig. 2). The $\Delta G_i(CF_2)$ values obtained for PEG-40M varied over the widest range: for lower homologs ($i = 1, 2$) these values are smaller than those for XE-60, while for higher homologs ($i = 4, 5$) they are greater than those for OV-101. Thus, increasing the polarity of the SP results in an increase in the nonadditivity of the $\Delta G_i(CF_2)$ contributions to the molar energy of sorption of the DMA PFA. It can be seen from the temperature dependence of $\Delta G_i(CF_2)$ (see Table 2) that under optimal analysis conditions the DMA PFA emerge from the column in the following order: $C_3F_7 \Leftrightarrow C_2F_5 < C_4F_9 \Leftrightarrow CF_3 < C_5F_{11} < C_6F_{13}$, and extrapolation to high analysis temperatures affords the order: $C_3F_7 < C_2F_5 < C_4F_9 < CF_3 < C_5F_{11} < C_6F_{13}$, *etc.*

Thus, an increase in the polarity of the SP (PEG-40M) results in an increase in the inversion of the retention times of DMA PFA and in a different retention order than that found for sorption by XE-60. We believe that, as in the case of XE-60, the decrease in the energy of sorption of a molecule by PEG-40M due to the introduction of the first and then the second CF_2 group is associated with the great contribution of the specific orientation (dipole-dipole) interaction of the polar SP and the polar sorbate, which is most probable for the sterically unhindered trifluoroacetamide. Increasing the length of the perfluoroalkyl chain prevents the most favorable spatial arrangement of the sorbate and the sorbent dipoles, which decreases the contribution of the orientation interaction to the molar energy of sorption, and results finally in lower retention times of the homologs with C_2F_5, C_3F_7, and even C_4F_9 groups than $CF_3C(O)NMe_2$. The $\Delta G_i(CF_2)$ contributions at $i \geq$ 4, 5 are due to the dispersion interaction of the CF_2 group with the SP and are comparable with $\Delta G_i(CF_2)$ (i = 4, 5) for the sorption of DMA PFA by OV-101.

The investigation of the energy of sorption on these phases made it possible to reveal the presence of inversion in the retention of amides and dimethylamides of perfluorocarboxylic acids and its characteristic features. The inversion of retention times is more noticeable in more polar stationary phases and at higher temperatures.

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