Novel way of separating polyfluorocarboxylic acids by ion-exclusion chromatography

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Abstract

Ion-exclusion chromatography has been successfully applied to the separation of a number of polyfluorocarboxylic acids. The separation of various mono- and dibasic polyfluorocarboxylic acids having a different alkyl group was investigated using a polymethacrylate-based weakly acidic cation-exchange resin (TSK gel OApak-A) in the H^+-form and conductimetric detection. When water was used as the eluent, polyfluorocarboxylic acids could not be resolved. When an aqueous solution of sulfuric acid, benzoic acid, o-phthalic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, and tartaric acid was used, the separation of polyfluorocarboxylic acids occurred for monobasic ones. While, for fluorine-containing dibasic acids, imperfect separation of peaks occurred. In order to improve their separation, the effect of an addition of organic modifiers such as methanol, 2,2,2-trifluoroethanol and 2H-hexafluoro-2-propanol in the eluent was also investigated. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyfluoro- or perfluorocarboxylic acids, which are industrially important materials for the preparation of fluoropolymers, fluorosurfactants, textile finishers and so on, have a unique character primarily associated with the presence of fluorine atom in the alkyl group when compared with that of usual carboxylic acids [1]. For example, due to the inductive effect of the fluorine atom in the alkyl group of carboxylic acid, the acidity of polyfluorocarboxylic acids increases with an increase of the number of fluorine atoms introduced in the alkyl group [2]. In addition, the perfluoroalkyl group shows a lower surface energy than the alkyl group [3]. Though the development of versatile analytical means is required for the polyfluorocarboxylic acids, their unique character such as strong acidity, low surface energy, and the strong hydrophobic property of polyfluoroalkyl group makes them difficult to analyze by means of conventional liquid chromatography.

Ion-exclusion chromatography with conductimetric detection is known as a useful technique for the separation of organic and inorganic weak acids [4–17]. Recently, this method has been successfully extended to the analysis of carboxylic acids [17]. Because the same derivatives can be used with the usual carboxylic acids and fluorine-containing ones, it seemed of interest to investigate their behavior in ion-exclusion chromatography. This study was undertaken in order to examine the application and limitation of the analysis for various types of poly-

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fluorocarboxylic acids by ion-exclusion chromatography.

2. Experimental

2.1. Apparatus

A Shimadzu ion chromatograph Model LC-10 (Kyoto, Japan) was used, which consisted of a system controller SCL-10A (Kyoto), a conductivity detector CDD-6A (Kyoto), a Model LC-10AD (Kyoto) eluent delivery pump with a Reodyne sample injector of 20 µl, a column oven CTO-10A (Kyoto) with a constant temperature controller at 40°C, a Model Shodex degasser (Tokyo, Japan), and a Chromatopac C-R6A (Kyoto) for data collection and processing.

2.2. Column

Two consecutively connected columns were used. Tosoh stainless column of TSKgel OApak-P (4 cm× 6.0 mm I.D.) (strong acidic cation-exchange resin) was used as the pre-column to remove the cationic species. As the separation column, Tosoh stainless column packed with TSKgel OApak-A (30 cm×7.8 mm I.D.) (polymethacrylate-based weakly acidic cation-exchange resin in the H^+ form with a particle size of 5 µm) was used. The column was equilibrated thoroughly with the eluent before the chromatographic run.

2.3. Reagents and solutions

2.3.1. Preparation of reagents

Standard solutions of nineteen sodium salts of monobasic and dibasic polyfluorocarboxylic acids were prepared. Sodium salts of trifluoroacetic acid (Wako, Osaka, Japan), trichloroacetic acid (Wako) and pentafluoropropionic acid (Aldrich, USA) were used as received. Except for monofluoroacetic acid, other fluorine-containing carboxylic acids like difluoroacetic acid, chlorodifluoroacetic acid and perfluorobutyric acid (all from PCR, USA), perfluorovaleric acid (Daikin), perfluorooctanoic acid (Tokem), 3H-tetrafluoropropionic acid (Daikin), 5H-octafluorovaleric acid (Daikin), 2,2-bis(trifluoromethyl)propionic acid (Daikin), 3,3,3-trifluoro-2-(trifluoromethyl)propionic acid (Daikin), perfluorosuccinic acid (PCR), 2,2-difluorosuccinic acid (PCR), perfluoroglutaric acid (PCR), perfluorosuberic acid (Daikin), perfluoroazelaic acid (Daikin) were purchased from commercial sources, and converted into corresponding Na salts by neutralization with an aqueous NaOH solution followed by evaporation to dryness and finally purified by recrystalization with a mixture of MeOH and CHCl$_3$. The ethyl ester of monofluoroacetic acid was prepared by the reaction of ethyl monochloroacetate with KF according to the literature method [18,19]. The corresponding Na salt was prepared by the reaction of its ethyl ester with powdered NaOH, which was then purified by recrystalization with a mixture of MeOH and CHCl$_3$. The concentration of each of standard solutions were adjusted to 20 ppm concentration and four mixtures of sample solutions (Groups 1–4) were made; the Groups consisted of mixtures of derivatives of (1) acetic acid, (2) perfluorocarboxylic acids having a perfluoroalkyl chain length of 1–7 carbon number, (3) polyfluorocarboxylic acids and (4) dibasic polyfluorocarboxylic acids. As a standard, sulfuric acid (2 ppm) was added. Thus, following four sample mixtures of carboxylic acids [$R_fC(O)ONa$ in Groups 1–3, $NaO(O)CR_fC(O)ONa$ in Group 4] were prepared:

Group 1: R_f=CF_3–(**1a**), CHF_2–(**1b**), CH_2F–(**1c**), $CClF_2$–(**1d**), CCl_3–(**1e**)

Group 2: R_f=CF_3–(**1a**), C_2F_5–(**2b**), n-C_3F_7–(**2c**), n-C_4F_9–(**2d**), C_6F_5–(**2e**), n-C_7F_{15}–(**2f**)

Group 3: R_f=CHF_2–(**1b**), $H(CF_2)_2$–(**3b**), $H(CF_2)_4$–(**3c**), $(CF_3)_2CH$–(**3d**), $(CF_3)_2C(CH_3)$–(**3e**)

Group 4: R_f=$-CH_2CF_2$–(**4a**), $-(CF_2)_2$–(**4b**), $-(CF_2)_2$–(**4c**), $-(CF_2)_6$–(**4d**), $-(CF_2)_7$–(**4e**)

2.3.2. Eluents

The eluents, consisting of sulfuric acid, benzoic acid, o-phthalic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, tartaric acid and organic solvents like methanol, 2,2,2-trifluoroethanol (F-Tech), 2H-hexafluoro-2-propanol (Central Glass), 2,2,3,3-tetrafluoropropanol (Daikin) and 2,2,3,3,3-pentafluoropropanol (Daikin), were

prepared by dissolving the acids and organic solvents in distilled, deionized water and filtering through a 0.45-μm membrane.

3. Results and discussion

3.1. Effect of various eluents on ion-exclusion chromatographic separation of polyfluorocarboxylic acids

In ion chromatography, water or aqueous solutions of sulfuric acid are generally used as eluents [4]. When water was used as an eluent in the present ion-exclusion chromatographic study, peaks of carboxylic acids of Groups 1–4 could not be resolved. When 1 mM sulfuric acid was used as an eluent, trifluoroacetic acid (**1a**) and difluoroacetic acid (**1b**) among acids of Group 1 eluted as a mixture. The appearance of a system peak just before these two peaks interfered with the good resolution of peaks

having low retention volumes (V_R). All peaks of polyfluoro-dibasic acids in Group 4 coeluted with sulfuric acid eluent. Therefore, in order to find a suitable weak organic acids eluent, analyses of sample solutions of Groups 1–4 were tested with 6 mM solutions of benzoic acid, o-phthalic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid and tartaric acid, respectively. Among these eluents, benzoic acid, o-phthalic acid, and tartaric acid afforded good results by considering such points as (1) the degree of the separation of peaks corresponding to each carboxylic acid, (2) the degree of the interference by the system peak and (3) the degree of the stability of the baseline. These results are summarized in Table 1.

For example, the separation of all perfluorocarboxylic acids of Group 2 could be achieved by using a solution of benzoic acid as an eluent (Fig. 1). It was found that the order of the elution of perfluorocarboxylic acids was in accordance with the increasing carbon number of the carboxylic acid. When other eluents were used for the analysis of Group 2, the

Table 1
Comparison of ion-exclusion chromatograms of Group 1–4 with various eluents

Eluents (conc.)	Group 1	Group 2	Group 3	Group 4	Other comments
Benzoic acid (6 mM)	Three peaks (**1a–c**) coeluted	Good separation	Two peaks (**1b, 3b**) coeluted	Five peaks (H$_2$SO$_4$, **4b–e**) coeluted Peak (**4e**) not detected	Peak (**3d**) split into two peaks BG[c] 359, pH 3.13 (19.3°C)
o-Phthalic acid (6 mM)	Good separation	Peak (**2f**) not detected	Good separation	Four peaks (H$_2$SO$_4$, **4b–d**) coeluted Peak (**4e**) not detected	BG 1226, pH 2.88 (16.5°C)
Benzenetri-carboxylic acid[a] (6 mM)	Good separation	Two peaks (**2f, 2e**) not detected	Two peaks (**3d, 3e**) not detected	Four peaks (H$_2$SO$_4$, **4b, 4c**) coeluted	Baseline drifted BG 1050, pH 2.85 (18.4°C)
Benzenetetra-carboxylic acid[b] (6 mM)	Two peaks (**1b, 1d**) coeluted	Two peaks (**2f, 2e**) not detected	Two peaks (**3d, 3e**) not detected	Four peaks (H$_2$SO$_4$, **4b, 4c**) coeluted	Baseline drifted BG 2694, pH 2.31 (18.4°C)
Tartaric acid (6 mM)	Two peaks (**1a, 1b**) coeluted. A peak (**1e**) not detected	Peak (**2f**) not detected	Good separation	Five peaks (H$_2$SO$_4$, **4b–e**) coeluted Peak (**4e**) not detected	System peak overlapped the peak of **2d** BG 1208, pH 2.66 (19.3°C)
Sulfuric acid (1 mM)	Three peaks (H$_2$SO$_4$, **1a, 1b**) coeluted	Two peaks (H$_2$SO$_4$, **1a**) coeluted. A peak (**2f**) not detected	Two peaks (H$_2$SO$_4$, **1b**) coeluted	Six peaks (H$_2$SO$_4$, **4a–e**) coeluted	Peak (**3d**) split into two peaks BG 1172 pH 2.75 (19.3°C)

[a] 1,3,5-Benzenetricarboxylic acid.

[b] 1,2,4,5-Benzenetetracarboxylic acid.
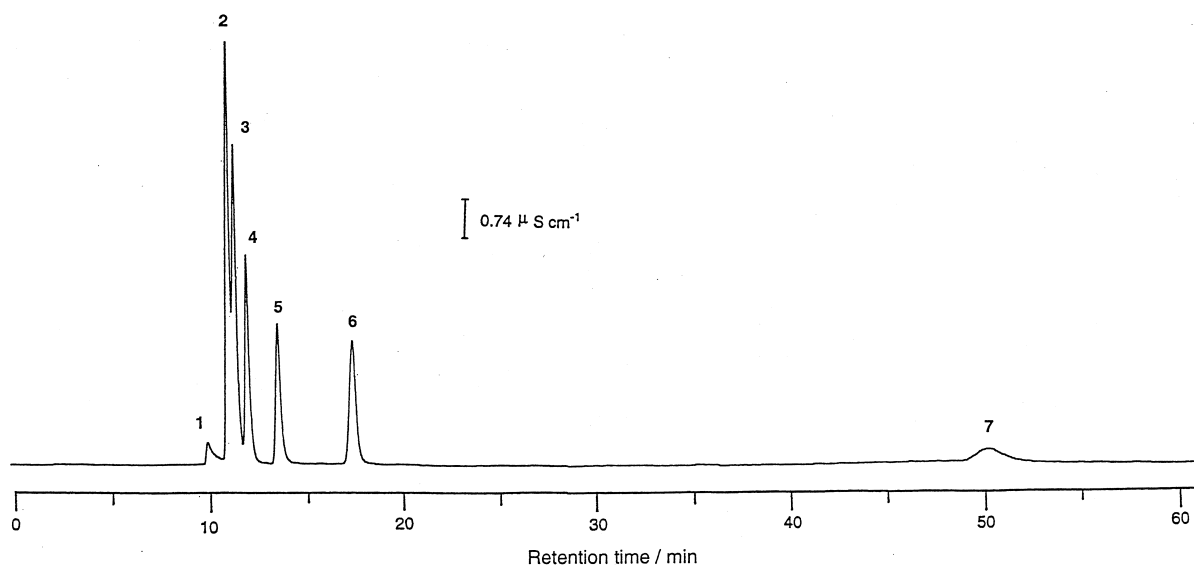
[c] Background, μS/cm.

Fig. 1. Ion-exclusion chromatogram of fluorine-containing carboxylic acids of Group 2 by elution with 6 m*M* benzoic acid. Column: TSKgel OApak-A (polymethacrylate-based weakly acidic cation-exchange resin in the H$^+$-form) (30 cm×7.8 mm I.D.), Column temperature: 40°C, flow-rate: 0.6 ml/min, sample concentration: sulfuric acid (2 ppm), polyfluorocarboxylic acids (20 ppm), conductimetric detection sensitivity: 1 mS/cm=10 mV. Peaks: 1=sulfuric acid, 2=**1a**, 3=**2b**, 4=**2c**, 5=**2d**, 6=**2e**, 7=**2f**.

peak of perfluorooctanoic acid (**2f**) which has a most strong hydrophobic character among acids in Group 2 did not appear under the comparable analytical conditions (6 m*M* elution concentration). Concerning the analysis of Group 1, the use of *o*-phthalic acid (Fig. 2) and 1,3,5-benzenetricarboxylic acid was found to afford successful resolution for each of acetic acid derivatives (**1a~e**). Samples of Group 3

could be separated when such eluents as *o*-phthalic acid (Fig. 3) and tartaric acid were used. Generally, a good result was obtained by using *o*-phthalic acid as eluent, as complete separation of peaks of Groups 1 and 3 could be achieved with this eluent. The dibasic acids of Group 4 eluted faster than the monobasic acids as is generally observed for hydrocarbonous dibasic acids [17]. However, peaks of the fluorine-
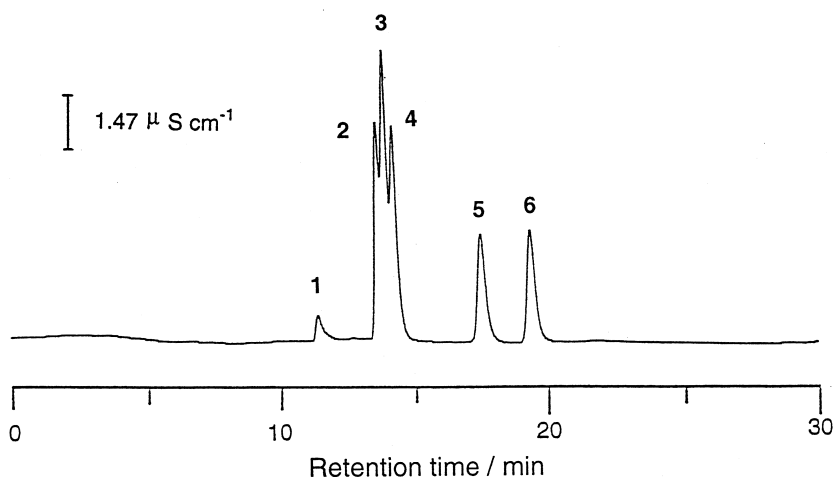

Fig. 2. Ion-exclusion chromatogram of fluorine-containing carboxylic acid of Group 1 by elution with 6 m*M o*-phthalic acid. Other chromatographic conditions were as described in Fig. 1. Peaks: 1=sulfuric acid, 2=**1a**, 3=**1b**, 4=**1d**, 5=**1e**, 6=**1c**.
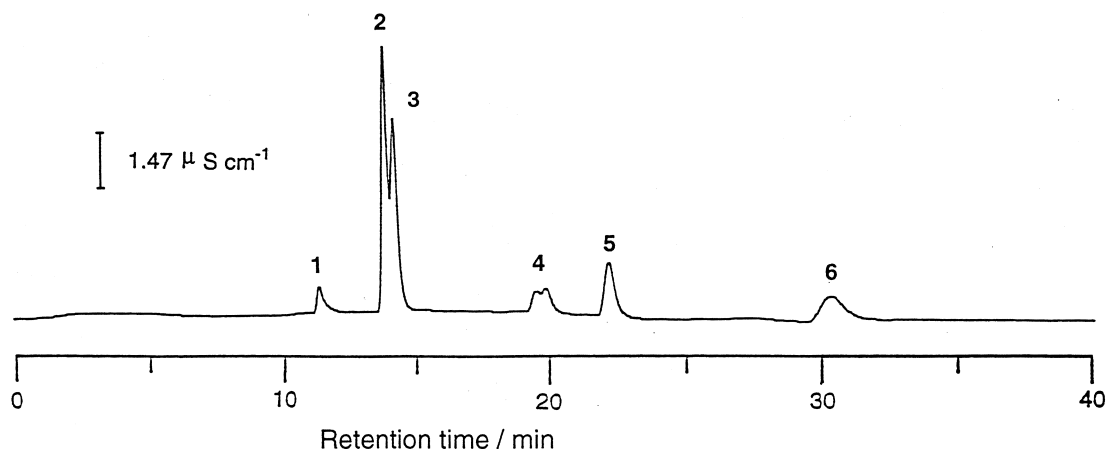
Fig. 3. Ion-exclusion chromatogram of fluorine-containing carboxylic acid of Group 3 by elution with 6 mM o-phthalic acid. Other chromatographic conditions as described in Fig. 1. Peaks: 1=sulfuric acid, 2=**1b**, 3=**3b**, 4=**3d**, 5=**3c**, 6=**3e**.

containing dibasic acids in Group 4 could be separated only incompletely from other analogues under the present chromatographic conditions. Peaks of **4a** and **4d** could be separated with a tartaric acid eluent from a united peak consisting of a mixture of sulfuric acid, **4b**, **4c** and **4e**.

The peak of 3,3,3-trifluoro-2-(trifluoromethyl)propionic acid (**3d**) was found to split into two peaks depending on the eluents used (see, for example, Fig. 3 and Tables 3–5). The relative height of the two split peaks (V_{R1} and V_{R2}) changed depending on the pH of the eluent also (Table 4). From these observa-

Table 2

Retention volumes and distribution coefficients of polyfluorocarboxylic acids with 6 mM o-phthalic acid; $K_d = (V_R - V_0)/V_i$; V_i is the volume of eluent inside the resin beads

Acid	V_R (ml)	K_d
Void (sulfuric acid)	6.8 (6.1)[a]	0
CH$_3$OH	12.0 (12.0)[a]	1
CF$_3$C(O)OH (**1a**)	8.1	0.25
CF$_2$HC(O) OH (**1b**)	8.3	0.29
CFH$_2$C(O)OH (**1c**)	11.5	0.90
CClF$_2$C(O)OH (**1d**)	8.5	0.33
CCl$_3$C(O)OH (**1e**)	10.4	0.69
C$_2$F$_5$C(O)OH (**2b**)	8.7	0.37
n-C$_3$F$_7$C(O)OH (**2c**)	9.8	0.58
n-C$_4$F$_9$C(O)OH (**2d**)	12.8	1.15
(structure) n-C$_7$F$_{15}$C(O)OH (**2f**)	21.4 (29.42)[a]	2.18 (3.95)[a]
H(CF$_2$)$_2$C(O)OH (**3b**)	8.5	0.33
H(CF$_2$)$_4$C(O)OH (**3c**)	13.2	1.23
(CF$_3$)$_2$CHC(O)OH (**3d**)	11.8	0.96
(CF$_3$)$_2$C(CH$_3$)C(O)OH (**3e**)	18.0	2.15
HO(O)CCH$_2$CF$_2$C(O)OH (**4a**)	8.3	0.29
HO(O)C(CF$_2$)$_2$C(O)OH (**4b**)	6.8	0
HO(O)C(CF$_2$)$_3$C(O)OH (**4c**)	6.8	0
HO(O)C(CF$_2$)$_6$C(O)OH (**4d**)	8.3	0.29
HO(O)C(CF$_2$)$_7$C(O)OH (**4e**)	6.8	0

[a] Calculated from the V_R data using 6 mM benzoic acid eluent.

tions, it was concluded that the splitting of the peak was ascribed to the existence of a rotational isomer of **3d** in the eluent. It was considered that the bulky 1,1,1,3,3,3-hexafluoropropyl group bonded to the carboxyl group resulted in the formation of barrier for the free rotation around the α-bond axis so that rotational isomers could be detected. We believe that this is the first case in which a rotational isomer was detected by ion-exclusion chromatography. Further study on the rotational isomers of such compounds as difluoroacetic acids having a bulky cyclic perfluoroamino group by ion-exclusion chromatography is under way.

3.2. Distribution coefficient of polyfluorocarboxylic acids

The retention volumes of polyfluorocarboxylic acids were measured with various organic acid eluents. Those calculated from the data with 6 m*M* o-phthalic acid eluent are shown in Table 2. The distribution coefficients were calculated assuming $V_R = 1.00$ for methanol [12]. Dissociation constants of polyfluorocarboxylic acids are higher than those of carboxylic acids due to the inductive effect of fluorine in proportion to the degree of the substitution of fluorine atoms. For example, trifluoroacetic acid ($K_a = 1.8$; $pK_a = -0.26$) is about 10^4 times stronger than acetic acid ($K_a = 1.75 \cdot 10^{-5}$; $pK_a = 4.76$) and four times stronger than trichloroacetic acid ($K_a = 0.23$; $pK_a = 0.64$) [2]. And yet, trifluoroacetic acid is not strong when compared with sulfuric acid [20]. It is considered that the higher analogues of polyfluorocarboxylic acids have almost the same order of dissociation constants as that of trifluoroacetic acid. It is known that distribution coefficient of carboxylic acids increases with an increase in the pK_a value [4,5,12]. Therefore, for the ion-exclusion chromatographic separation of most polyfluoroacetic acids which have small pK_a values, it was considered that an ion-exclusion effect is the predominant factor. Table 2 shows that the V_R values of fluorinated acetic acids were in the order of **1a**<**1b**<**1c**, which is in accordance with an increase of pK_a values. As trichloroacetic acid (**1e**) is a weaker acid than trifluoroacetic acid (**1a**), it is considered to be more liable to be affected by the hydrogen ion concentration (see for example Table 3). Furthermore, since the chlorine atom is more hydrophobic

than the fluorine atom, **1e** interacted with the column resin more strongly than **1a**, which resulted in the larger V_R value for the former.

For several dibasic perfluorocarboxylic acids (**4b**, **4c** and **4e**), V_R values were found to be almost zero with o-phthalic acid eluent. For polyfluorocarboxylic acids having stronger hydrophobicity such as perfluorooctanoic acid (**2f**), perfluorobenzoic acid (**2e**), 5H-octafluorovaleric acid (**3c**) and 2,2-bis(trifluoromethyl)propionic acid (**3e**), an adsorption effect towards column resin seems to major factor for their high V_R values.

3.3. Effect of concentration of several eluents on retention volumes of carboxylic acids

In order to examine the effect of the concentration of eluent on the retention volume of fluorine-containing carboxylic acids, ion-exclusion chromatographic separation of Groups 1–4 was carried out with several concentrations of eluents such as sulfuric acid, benzoic acid and o-phthalic acid in the ranges of 0.1–1.0 m*M* for sulfuric acid, 1–8 m*M* for benzoic acid and 2–10 m*M* for o-phthalic acid. The relationships between the concentration of eluents and the V_R values of carboxylic acids of Groups 1–4 are shown in Table 3.

It was found that V_R values of acids increased with an increase in the concentration of sulfuric acid eluents. Furthermore, the perfluorooctanoic acid peak (**2f**), which did not appear with 1 m*M* sulfuric acid as eluent, could be detected with the lower concentration of 0.1–0.5 m*M* sulfuric acid.

Similarly to the sulfuric acid eluent, the V_R values of acids of Groups 1~4 increased with an increase of the concentration of benzoic acid eluents. As the peak of 2,2-bis(trifluoromethyl)propionic acid (**3d**) split into two peaks, V_R values were determined for each of the two peaks. The difference in the V_R values of these two peaks was independent of the concentration of benzoic acid eluent. Among the acids of Group 4, the peaks of 2,2-difluorosuccinic acid (**4a**) and perfluorosuberic acid (**4d**) could be separated from those of other acids with a 6–8 m*M* concentration of benzoic acid eluent.

As was observed in the case of sulfuric acid eluent, V_R values of acids of Groups 1–4 also increased with an increase of the concentration of o-phthalic acid eluents. Among acids of Group 4,

Table 3
Effect of concentration of eluents volumes (V_R) of fluorine-containing carboxylic acid

Sample		Eluents (mM)													
		Sulfuric acid				Benzoic acid					o-Phthalic acid				
		0.1	0.25	0.5	1	1	2	4	6	8	2	4	6	8	10
H_2SO_4 (V_R)		5.9	6.2	6.6	7.5	5.9	6.0	6.1	6.1	6.2	6.2	6.6	6.8	6.9	7.1
Group 1	1a	6.3	6.8	7.5	8.2	6.3	6.4	6.6	6.8	6.9	7.3	7.9	8.1	8.3	8.5
	1b			7.6							7.3	7.9	8.3	8.5	8.8
	1c	7.2	8.5	9.7	11.3	6.9	7.5	8.1	8.5	8.9	9.9	11.0	11.5	11.9	12.1
	1d	6.3	6.8	7.7	8.5						7.4	8.1	8.5	8.7	8.9
	1e	6.6	7.4	8.5	10.5	6.5	6.9	7.2	7.5	7.7	8.6	9.8	10.4	10.9	11.2
Group 2	1b	6.3	6.7	7.2	8.1	6.2	6.4	6.6	6.7	6.8	6.9				
	2b		6.9	7.6	8.7		6.6	6.7	6.9	7.0	7.6	8.3	8.7	9.0	9.2
	2c	6.5	7.2	8.2	10.0	6.3	6.8	7.0	7.3	7.4	8.3	9.2	9.8	10.2	10.4
	2d	6.9	8.2	10.1	13.4	6.7	7.4	7.8	8.2	8.5	10.2	12.0	12.8	13.5	13.9
	2e	7.9	10.5	14.1	20.9	7.4	8.3	9.4	10.2	10.9	14.8	18.6	21.4	23.4	25.0
	2f	18.1	34.6	59.7	−[b]	16.4	21.0	26.2	29.4	31.9	−	−	−	−	−
Group 3	1b	6.3	6.8	7.3	8.2	6.2	6.4	6.6	6.8	6.9	7.3	7.9	8.3	8.5	8.8
	3b			7.5	8.5						7.5	8.1	8.5	8.8	8.9
	3c	6.9	8.3	10.3	13.8	7.0	7.3	7.9	8.3	8.6	11.0	12.2	13.2	13.9	14.4
	3d[a]	7.1	8.5	9.9	8.5	6.9	7.5	8.2	8.6	9.0	10.1	11.1	11.6	11.9	12.1
		8.3	9.7	10.8	11.4	7.9	8.6	9.3	9.8	10.1	11.0	11.6	11.8	19.6	
	3e	7.5	9.4	11.7	12.3	7.1	7.8	8.6	9.3	9.8	12.8	15.9	18.0	19.6	20.8
Group 4	4a	6.2	6.7	7.3	8.2	6.1	6.3	6.5	6.7	6.8	7.3	7.9	8.3	8.6	8.8
	4b														
	4c	6.0	6.1	6.6	7.6	5.9	5.9	6.0	6.0	6.1	6.2	6.5	6.8	6.9	7.0
	4d										6.8	7.6	8.3	9.6	9.1
	4e								6.2	6.2	6.2	6.5	6.8	6.9	7.0
BG (mS/cm)		138	329	615	1172	114	176	265	335	398	616	957	1226	1443	1635

[a] Peak (3d) split into two peaks.
[b] −: Very large V_R.

peaks of 2,2-difluorosuccinic acid (4a) and per-fluorosuberic acid (4d) could be separated with o-phthalic acid eluent, the order being reversed at 6 mM. The V_R of 4d became larger than that of 4a when higher concentration than 6 mM o-phthalic acid eluent was used.

3.4. Effect of pH of o-phthalic acid used as the eluent on retention volumes of carboxylic acids

In order to examine the effect of the pH of o-phthalic acid eluent on the retention volume of fluorine-containing carboxylic acids, ion-exclusion chromatographic separation of those of Groups 1–4 was investigated in the range pH 2.88–3.29. The relationships between the pH of o-phthalic acid and the V_R values of carboxylic acids of Groups 1–4 are shown in Table 4. It was observed that the V_R decreased with an increase of pH of o-phthalic acid eluent as was observed for the hydrocarbonous carboxyolic acids [17].

3.5. Calibration graphs of fluorine-containing carboxylic acid

Under the chromatographic conditions with 6 mM

Table 4

Effect of pH of *o*-phthalic acid eluent on retention volumes (V_R) of fluorine-containing carboxylic acids

Sample		pH				
		2.88	2.97	3.02	3.11	3.29
Group 1	**1a**	8.2	8.1	8.1	} 8.2	} 8.1
	1b	8.4	8.3	8.3		
	1c	11.7	11.6	11.5	11.4	11.0
	1d	8.7	8.5	8.5	8.5	8.4
	1e	10.7	10.5	10.5	10.4	10.1
Group 2	**1a**	8.2	8.1	8.1	8.0	8.0
	2b	8.9	8.7	8.7	8.7	8.5
	2c	13.1	12.9	10.9	12.7	12.1
	2d	10.0	9.9	9.8	9.7	9.5
	2e	22.0	21.6	21.4	20.5	19.8
	2f	–[b]	–	–	–	–
Group 3	**1b**	8.4	8.3	8.3	8.2	8.1
	3b	8.0	8.5	8.5	8.5	8.4
	3c	14.0	13.3	13.3	13.1	12.6
	3d[a]	11.6	11.7	11.6	11.5	11.2
		11.8	11.9	11.9	11.9	11.8
	3e	18.4	18.2	18.1	17.7	15.8
Group 4	**4a**	8.5	8.3	8.3	8.2	7.9
	4b	}	}	}	}	}
	4d	6.9	6.8	6.8	6.8	6.7
	4e					
BG (µS/cm)		1226	1215	1218	1173	1053

[a] Peak (3d) split into two peaks.

[b] Very large V_R.

o-phthalic acid eluent, calibration graphs were obtained by plotting the peak area of polyfluorocarboxylic acids vs. the concentration (Fig. 4). Peak areas (mV s) were obtained by varying the concentration from 2 to 100 ppm for each of single acid sample solution. Because of the disappearance of the peak of perfluorooctanoic acid (**2f**) due to its very high retention volume (V_R), the graph (B) of Fig. 4 was plotted without the data of **2f**. Furthermore, in the case of dibasic acid, the calibration graphs were made only for 1,1-difluorosuccinic acid (**4a**) and perfluorosuccinic acid (**4b**) as the retention volumes of perfluoroglutaric acid (**4c**), perfluorosuberic acid (**4d**) and perfluoroazelaic acid (**4e**) coincided with that of **4b**. Thus, linear relationship was obtained for these acids of Groups 1–4 in the range of 2–100 ppm concentration.

3.6. Effect of organic modifier

It is known that the addition of an organic modifier can reduce the adsorption effects of hydrophobic carboxylic acids to the cation-exchange resin and thus decrease their V_R values. So, in order to accelerate the elution of polyfluorocarboxylic acids with a high hydrophobic nature, the effect of the addition of organic modifier was examined. In the present work, not only methanol but also polyfluoroalcohols like trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,3,3-tetrafluoropropanol, 2,2,3,3,3-pentafluoropropanol were examined. However, no remarkable difference was observed in the V_R values of polyfluorocarboxylic acids irrespective of the kind of polyfluoroalcohols used except for the interference due to the system peaks. Therefore, as representative
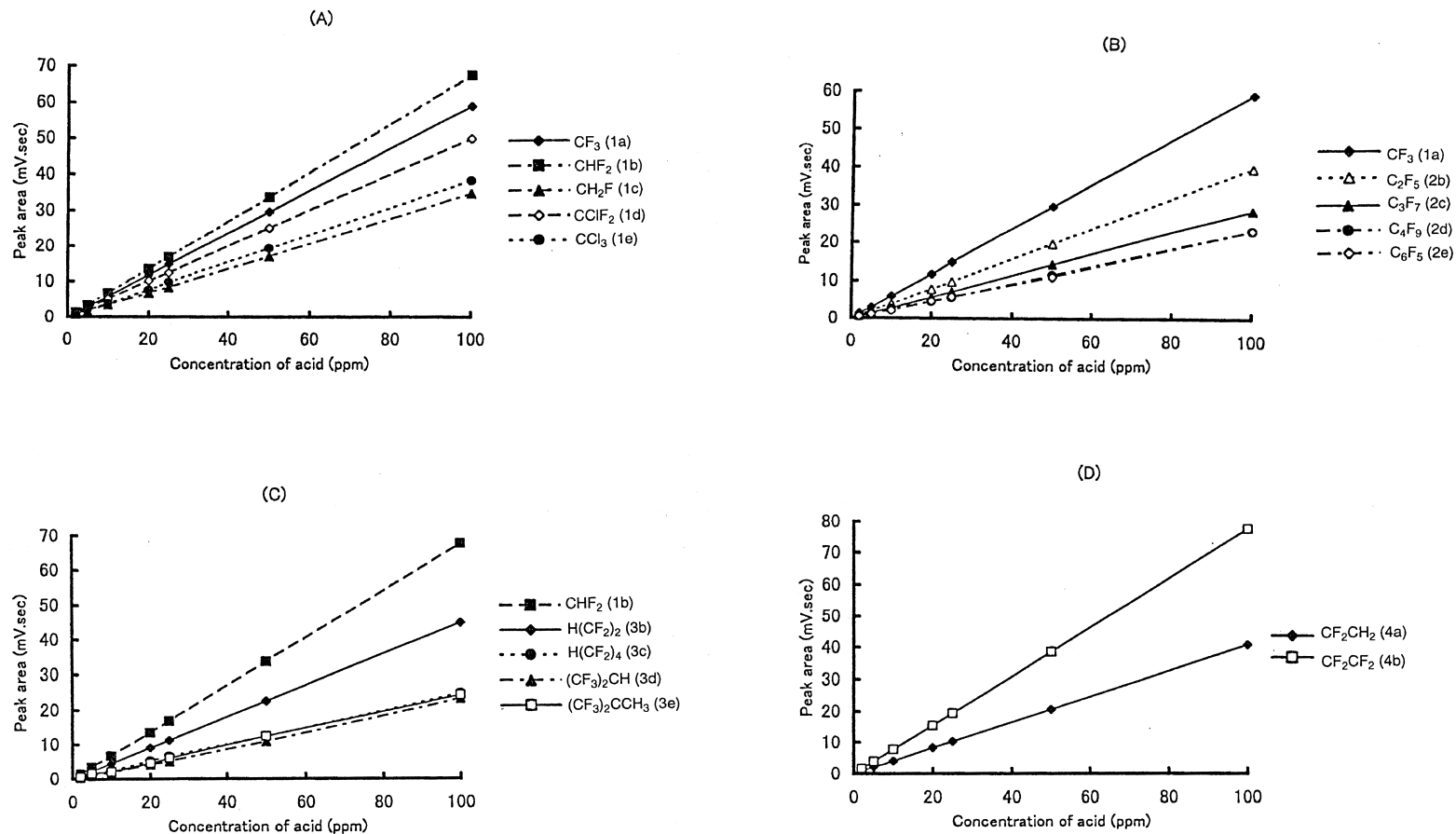
Fig. 4. Calibration curve of a mixture of fluorine-containing carboxylic acids in the range of 2–100 ppm by elution with 6 mM o-phthalic acid. Other chromatographic conditions as described in Fig. 1.

examples for studying the effect of an addition of fluoroalcohols, two cases using trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol are described. The effect of the addition of methanol, trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol to *o*-phthalic acid eluent are summarized in Table 5. It was observed that the V_R decreased with an increase of the amount of the modifier as was observed for usual hydrocarbonous carboxylic acid [17]. Furthermore, it was found that the peak of perfluorooctanoic acid (**2f**), of which peak did not appear without an addition of any organic modifier, could be detected by adding either more than 5% methanol or 10% fluoroalcohol successfully.

4. Conclusion

The ion-exclusion chromatography of polyfluorocarboxylic acids was investigated using a column of TSKgel OApak-A, weakly acidic cation-exchange resin. Good resolution of carboxylic acids was accomplished for monobasic acids by elution with organic acid solutions, while in the case of dibasic

Table 5
Effect of concentration of modifiers in eluent on retention volumes (V_R) of fluorine-containing carboxylic acids

Sample		Eluent (%)													
		Methanol				1,1,1-Trifluoroethanol					1,1,1,3,3,3-Hexafluoroisopropanol				
		5	10	15	20	0.5	1	2	5	10	0.5	1	2	5	10
Alcohol (V_R)		11.8	11.7	11.7	11.6	17.3	17.1	16.8	16.3	15.5	44.8	45.0	43.6	30.8	17.0
Group 1	**1a**	8.0	8.0	7.9	7.9	8.1	8.1	8.0	7.9	7.7	8.0	7.9	7.6	7.3	6.8
	1b	8.2	8.3	8.2	8.2	8.2	8.3	8.2	8.1	7.9	8.2	8.1	7.9	7.4	7.0
	1c	11.5	11.7	11.6	11.6	11.4	11.4	11.3	11.1	10.8	11.2	11.0	10.6	9.7	9.2
	1d	8.4	8.3	8.2	8.2	8.4	8.5	8.4	8.1	7.9	8.3	8.2	7.9	7.4	} 7.0
	1e	10.1	9.8	9.6	9.4	10.2	10.2	10.0	9.5	8.8	9.7	9.4	8.7	7.6	
Group 2	**1a**	8.0	8.0	7.9	7.9	8.1	8.1	8.0	7.9	7.7	8.0	7.9	7.7	7.2	6.8
	2b	8.6	8.5	8.4	8.3	8.6	8.7	8.6	8.4	8.2	8.5	8.5	8.3	7.7	7.2
	2c	9.5	9.3	9.1	8.9	9.6	9.7	9.6	9.4	9.1	9.6	9.6	9.6	9.0	8.4
	2d	12.0	11.4	10.9	10.4	12.5	12.6	12.3	11.9	11.3	12.5	13.1	13.9	14.2	12.1
	2e	19.5	18.1	16.9	15.9	20.5	20.1	19.3	17.9	16.3	19.4	19.3	18.4	17.4	15.1
	2f	52.2	51.0	39.2	29.5	–[c]	–	–		54.0	–	–	–	–	58.0
Group 3	**1b**	8.2	8.2	} 8.2	} 8.2	8.2	8.2	8.2	8.2	} 7.9	8.1	8.0	} 7.9	} 7.4	} 7.0
	3b	8.4	8.3			8.4	8.4	8.3	8.2		8.2	8.2			
	3c	11.5	11.7	11.4	10.9	12.7	12.8	12.4	11.6	10.5	12.0	11.9	11.2	9.6	8.6
	3d[a]	11.7[b]	11.7[b]	11.7[b]	11.7[b]	11.5	11.4	11.2	10.8	10.1	11.0	10.7	10.0	8.8	8.0
						11.7	11.7	11.7	11.5	11.0	11.5	11.3	10.7	9.6	8.6
	3e	17.1	16.4	15.7	15.1	17.3	16.9	16.5	16.3	SP[d]	16.1	16.5	17.5	17.3	SP
Group 4	**4a**	8.3	8.2	8.2	8.2	8.1	8.2	8.2	8.0	7.8	8.0	7.9	7.7	7.1	6.7
	4b														
	4c	} 6.7	} 6.7	} 6.7	} 6.6	} 6.7	} 6.7	} 6.7	} 6.6	} 6.5	} 6.7	} 6.6	} 6.5	} 6.2	} 5.9
	4d														
	4e	7.9	7.6	7.4	7.2	7.9	8.1	7.9	7.5	7.0	7.7	7.6	7.2	6.5	6.2
BG (µS/cm)		1054	899	769	656	1202	1183	1144	1034	869	1202	1184	1144	1027	848

[a] Peak (**3d**) split into two peaks.
[b] This peak coincided with the methanol peak.
[c] Very large V_R.
[d] SP: system peak.

ones, it was difficult to separate them under the present analytical conditions. The present investigation has widened the applicability of ion-exclusion chromatography to the analysis of polyfluorocarboxylic acids.

Acknowledgements

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