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## Factor analysis in ion chromatography of carboxylate ions

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### Abstract

The retention times of five carboxylate ions (formate, acetate, propionate, *n*-butanoate and *n*-pentanoate) in ion chromatography were determined using 25 eluents prepared from NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>. Principal component analysis (PCA) and correspondence factor analysis (CFA) were applied to describe the behaviour of the carboxylate anions and the influence of the carbonate concentration of the eluents. With PCA, only one factor is necessary to model the retention times of each ion studied. CFA offers an analysis of second-order effects and shows how the selectivities of the chromatographic systems are modified with either the carbonate concentration or the concentration ratio of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>.

### 1. Introduction

There is great interest in the chemometric analysis of large sets of chromatographic data [1,2]. The process and applications of factor analysis [3] to gas chromatography (GC) [4–9] and liquid chromatography (LC) [10–14] have been particularly developed in the last two decades. Chemometric analysis of chromatographic retention data can be useful at two levels: for an overall view, through the variation of retention indices in GC or capacity factors in LC, and for an in-depth analysis of the behaviour of compounds through the selectivity parameters of the chromatographic systems.

Principal component analysis (PCA) is appropriate to give an overall view of chromatographic data [4,5,10,11,14], *e.g.*, to show independence of the mechanism between normal-phase and reversed-phase liquid chromatography [14]. A more in-depth analysis is possible with correspondence factor analysis (CFA) [6–9,12–14], which is particularly appropriate for studying second-order effects, responsible for the selectivity in a given retention mechanism.

The ion chromatography (IC) of organic ions with a hydrophilic polar group and a hydrophobic part or chain involves a mechanism that is not easy to understand and to handle in order to optimize the selectivity [15,16]. Hence, the extension of the application of factor analysis in GC or LC retention data processing to IC became desirable. The need was simultaneously to delineate the potential interest in factor analy-

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sis for data processing of IC retention data and to gain a deeper insight into the behaviour of organic ions in IC. This was confirmed recently with a systematic study of parameters that could influence the retention of peptides and proteins in IC [17].

In this work, the retention times ( $t_R$ ) of a model series of five carboxylate anions ( $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_2\text{H}_5\text{COO}^-$ ,  $\text{C}_3\text{H}_7\text{COO}^-$  and  $\text{C}_4\text{H}_9\text{COO}^-$ ) using 25 carbonate eluents were determined. The corresponding data matrix was submitted to factor analysis by using PCA and CFA successively in order to evaluate the complexity of the retention mechanism and search for optimization. With PCA, the stress is placed on modelling the retention times of anions, and with CFA, the stress is placed on the relative behaviour of the anions and on the delineation of all the tenuous factors that govern it.

## 2. Experimental

The ion chromatograph used was an Eesti TASK Model IVK-21 equipped with a conductivity detector, an HIKS-1 separation column (150 × 3 mm I.D.) and a KU-2 suppressor column (250 × 4 mm I.D.). The eluents were  $\text{NaHCO}_3$  (0–0.9 mM)– $\text{Na}_2\text{CO}_3$  (0.2–1.2 mM) solutions delivered at 1.6 ml/min. The HIKS-1 resin is based on a methacrylic matrix, a copolymer of 2-hydroxyethyl methacrylate and ethylene dimethacrylate, and has a pellicular coated surface consisting of an ion exchanger:  $-\{\text{CH}_2\text{CH}[\text{C}_6\text{H}_4\text{CH}_2\text{N}^+(\text{CH}_3)_3]\}_m$ .

The general formula of the studied anions is  $\text{H}(\text{CH}_2)_n\text{COO}^-$ , with values of  $n$  ranging from 0 to 4. The aqueous solutions of the corresponding organic acids injected contained 1–10 · 10<sup>-3</sup> g l<sup>-1</sup> of the compounds  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{C}_2\text{H}_5\text{COOH}$ ,  $n\text{-C}_3\text{H}_7\text{COOH}$  or  $n\text{-C}_4\text{H}_9\text{COOH}$ . The sample volume was 0.1 ml. Analytical-reagent grade reagents and doubly distilled water were used. The retention times measured are presented in Table 1. The void time of the system used was 94 s.

Table 1

Retention times (s) of carboxylate ions on the HIKS-1 resin for various carbonate eluents with different concentrations  $C$  and ratios  $Z$

$Z = \frac{C_{\text{NaHCO}_3}}{C_{\text{Na}_2\text{CO}_3}}$	Anion	$C = C_{\text{Na}_2\text{CO}_3} + C_{\text{NaHCO}_3}$ (mM)				
		0.2	0.4	0.6	0.8	1.2
3.0	$\text{HCOO}^-$	374	258	218	202	179
	$\text{CH}_3\text{COO}^-$	354	245	204	188	172
	$\text{C}_2\text{H}_5\text{COO}^-$	432	280	231	208	183
	$\text{C}_3\text{H}_7\text{COO}^-$	450	305	250	226	197
	$\text{C}_4\text{H}_9\text{COO}^-$	588	405	322	295	247
1.0	$\text{HCOO}^-$	340	222	197	180	162
	$\text{CH}_3\text{COO}^-$	294	212	192	176	156
	$\text{C}_2\text{H}_5\text{COO}^-$	326	250	212	185	168
	$\text{C}_3\text{H}_7\text{COO}^-$	370	261	245	203	185
	$\text{C}_4\text{H}_9\text{COO}^-$	496	335	298	260	236
0.5	$\text{HCOO}^-$	280	210	185	171	157
	$\text{CH}_3\text{COO}^-$	264	202	179	161	150
	$\text{C}_2\text{H}_5\text{COO}^-$	286	222	192	176	160
	$\text{C}_3\text{H}_7\text{COO}^-$	315	254	215	194	176
	$\text{C}_4\text{H}_9\text{COO}^-$	442	322	284	256	228
0.33	$\text{HCOO}^-$	273	203	181	168	155
	$\text{CH}_3\text{COO}^-$	250	196	170	161	148
	$\text{C}_2\text{H}_5\text{COO}^-$	274	217	185	171	158
	$\text{C}_3\text{H}_7\text{COO}^-$	304	250	204	192	172
	$\text{C}_4\text{H}_9\text{COO}^-$	422	310	275	245	226
0.0	$\text{HCOO}^-$	235	194	174	159	147
	$\text{CH}_3\text{COO}^-$	230	172	166	155	144
	$\text{C}_2\text{H}_5\text{COO}^-$	250	200	180	168	156
	$\text{C}_3\text{H}_7\text{COO}^-$	279	218	202	181	171
	$\text{C}_4\text{H}_9\text{COO}^-$	385	302	268	241	223

## 3. Data processing

### 3.1. Principal component analysis

The retention times  $t_{i,j}$  for every ion ( $i$ ) studied with  $j$  eluents vary by a factor of 2–3 (Table 1).

The matrix of the normalized retention times  $[D]$  was submitted to PCA [3] to calculate the row and column vectors,  $R_k$  and  $C_k$ , respectively, in order to recalculate  $[D]$  as

$$[D] = \sum_1^k R_k C_k$$

where  $k$  is the number of abstract factors in the new and reduced hyperspace.

### 3.2. Correspondence factor analysis

With the original data matrix, a new matrix  $X_{ij}$  was constructed which was formed with the elements  $x_{i,j}$  [7,18,19]:

$$x_{i,j} = \frac{t_{i,j} - t_i \cdot t_j}{\sqrt{(t_i \cdot t_j)}}$$

where

$$t_i = \sum_{j=1}^{j=p} t_{i,j} \quad \text{and} \quad t_j = \sum_{i=1}^{i=n} t_{i,j}$$

Then the variance data matrix was calculated in order to determine the set of eigenvalues and the related eigenvectors.

The symmetrical role of the variables  $i$  and  $j$  must be emphasized [7]. It allows the superposition on the same graph of the projections of the row-points in the reduced hyperspace of the columns and, reciprocally, the projections of the column-points in the reduced hyperspace of the rows.

## 4. Results and discussion

The retention times of the five carboxylate ions, given in Table 1, follow regular trends:

(i) For the same ionic strength, the retention time of the carboxylate ions increases with R varying from Me to *n*-Bu.

(ii) The retention time of the formate ion is between those for acetate and propionate ions. It is outside the relatively regular deviation of the retention time as is often seen with the first member of a series.

(iii) With increase in the concentration of carbonate eluents  $C$ , all the carboxylate ions follow a classical trend, *i.e.*, a decrease in their retention time. This is accompanied simultaneously by a decrease in the amplitude of the variation between the less retained acetate ion and the more retained ion, pentanoate. A simultaneous decrease in the selectivity between any pair of given compounds is also observed.

(iv) For a given value of  $C$ , a decrease in the ratio  $Z$  of the carbonate eluents, which corre-

sponds to a relative increase in the concentration of the  $\text{Na}_2\text{CO}_3$  eluent, induces a decrease in all the retention times. This decrease is similar to the preceding one, but with a lower sensitivity. With the previous decrease in  $Z$ , which induces a decrease in the retention times, the selectivity between given pairs of the carboxylate ion, with  $R = \text{Me}$  up to *n*-Bu, remains relatively constant in most instances, but not all.

(v) Variations of selectivity between pairs of carboxylate ions are more sensitive to variations of the  $C$  term than to the  $Z$  term.

(vi) Nevertheless, when looking at relative decreases in retention data when  $C$  increases for the same  $Z$  value and the same ion, or when comparing the evolution of selectivity for a given ion pair when  $Z$  decreases for the same  $C$  value, more subtle variations are seen outside the above general trends. This motivated a more quantitative examination of the experimental results, on a statistical basis, *i.e.*, with multivariate analysis.

### 4.1. Principal component analysis

To obtain an overall view of the main trends governing the retention, the data set was configured as the data matrix presented in Table 2, and submitted to PCA. This second matrix has  $i$  rows corresponding to the combination of the  $C$  and  $Z$  terms and  $j$  columns corresponding to the carboxylate ions. Within the estimated experimental errors ( $\pm 2\%$ ), only one main factor is necessary to calculate the retention times. This simple relationship suggests that only a major retention mechanism is responsible for the observed retention times. This is in agreement with the relatively regular trends mentioned previously when considering the retention times, *i.e.*, the fairly good proportionality between the behaviour of the different carboxylate ions.

### 4.2. Correspondence factor analysis

In a second step, to analyse the secondary-order effects on retention, which are hidden by the above classical effect of the carbonate eluent concentrations, a CFA was undertaken. The

Table 2  
First reorganization of the original IC retention data matrix of the carboxylate ion for the CFA study

Label	Z	C	HCOO <sup>-</sup>	CH <sub>3</sub> COO <sup>-</sup>	C <sub>2</sub> H <sub>3</sub> COO <sup>-</sup>	C <sub>3</sub> H <sub>7</sub> COO <sup>-</sup>	C <sub>4</sub> H <sub>9</sub> COO <sup>-</sup>
1	3.0	0.2	} Retention times as in Table 1				
2	3.0	0.4					
3	3.0	0.6					
4	3.0	0.8					
5	3.0	1.2					
6	1.0	0.2					
7	1.0	0.4					
8	1.0	0.6					
9	1.0	0.8					
10	1.0	1.2					
11	0.5	0.2					
12	0.5	0.4					
13	0.5	0.6					
14	0.5	0.8					
15	0.5	1.2					
16	0.33	0.2					
17	0.33	0.4					
18	0.33	0.6					
19	0.33	0.8					
20	0.33	1.2					
21	0.00	0.2					
22	0.00	0.4					
23	0.00	0.6					
24	0.00	0.8					
25	0.00	1.2					

The carboxylate ions correspond to the column of this new matrix. The rows of this matrix correspond to the combination of the Z and C terms.

original experimental data matrix (Table 1) was modified in the form of a second matrix, given in Table 2, to make a better distinction between the variables corresponding to the composition of the eluent and the variables corresponding to the considered carboxylate ions.

This modified matrix was submitted to CFA. The row-points (the C and Z combinations) and the column-points (the studied anions) are projected simultaneously on the first factorial plane, defined by the axes 1 and 2 in Fig. 1, and which represents 78% of the information content. These axes 1 and 2 correspond to 44% and 34%, respectively, of the total information content. The relative behaviour of the carboxylate ions and the relative influences of the eluents are clearly taken into account by this first factorial plane.

On this map, we have drawn five clusters

where the projected row-points correspond to the same value of the eluent concentration C. The five clusters are ordered along the second bisector with a progressive increase from C = 0.2, in the left corner of the graph, up to C = 1.2, in the right corner. The dispersion of the row-points inside these clusters also shows the simultaneous and different contributions of the Z ratio according to the considered C values. A higher dispersion of the row-points for clusters C = 0.2 and 0.4 is observed. This is related to the higher selectivity at these lower C values, *i.e.*, at this lower ionic strength.

The projections of the five anions according to axis 1 go from the right side, with CH<sub>3</sub>COO<sup>-</sup>, up to the left side, with C<sub>4</sub>H<sub>9</sub>COO<sup>-</sup>. Even if the behaviour of the carboxylate ions, for example, through modification of the selectivity of the chromatographic system, could be dependent on

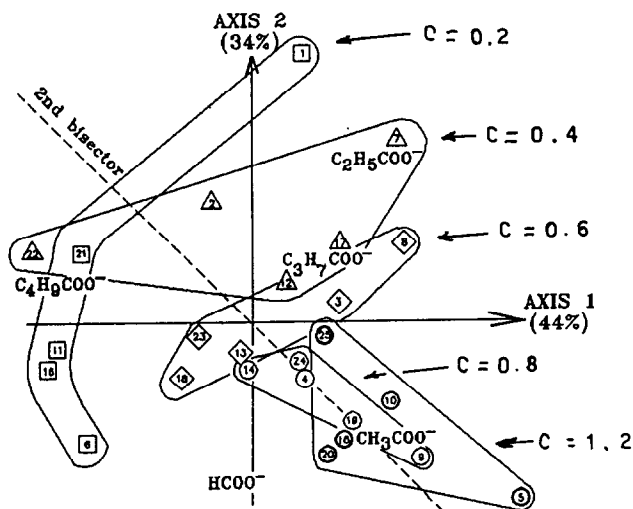


Fig. 1. CFA map of the five carboxylate ions studied with 25 chromatographic systems. The carboxylate ions correspond to the columns and the chromatographic systems to the rows of the considered data matrix (cf., Table 2). Simultaneous projection of the carboxylate ions and chromatographic systems on the first factorial plane defined by axes 1 and 2. The clusters delineate the different concentrations  $C$  of the eluents. The points inside these clusters correspond to the different  $Z$  values, from  $Z = 0$  up to 3.0.

the length of the alkyl chain, no special regularities can be seen according to axis 1 or 2. This suggests that the contribution of the alkyl chain to the retention mechanism is not simple.

The original data matrix was reorganized according to Table 3 to give a third matrix, with an organization only slightly different, from Table 1, for the row-points. Now, the columns correspond to the concentrations of the eluent, from  $C = 0.2$  up to 1.2. The rows correspond to the different carboxylate ions with their various values of the  $Z$  ratio, from 0 up to 3.

The simultaneous projections of the column-points and row-points are given in Fig. 2. Axes 1 and 2 represent 88% and 8% of the information content, respectively. The first factorial plane now represents 96% of the total information content. (This time, axis 1 corresponds to a more evident main axis of inertia.)

All the column-points and row-points are ordered regularly according to axis 1. Five clusters can also be delineated but for similar  $Z$

Table 3  
Second reorganization of the original IC retention data matrix of the carboxylate ion for the CFA study

Label	Ion	Z	C				
			0.2	0.4	0.6	0.8	1.2
1	HCOO <sup>-</sup>	3.0	} Retention times as in Table 1				
2		1.0					
3		0.5					
4		0.33					
5		0.00					
6	CH <sub>3</sub> COO <sup>-</sup>	3.0					
7		1.0					
8		0.5					
9		0.33					
10		0.00					
11	C <sub>2</sub> H <sub>5</sub> COO <sup>-</sup>	3.0					
12		1.0					
13		0.5					
14		0.33					
15		0.00					
16	C <sub>3</sub> H <sub>7</sub> COO <sup>-</sup>	3.0					
17		1.0					
18		0.5					
19		0.33					
20		0.00					
21	C <sub>4</sub> H <sub>9</sub> COO <sup>-</sup>	3.0					
22		1.0					
23		0.5					
24		0.33					
25		0.00					

The rows correspond to the carboxylate ions, from HCOO<sup>-</sup> up to C<sub>4</sub>H<sub>9</sub>COO<sup>-</sup>, eluted with different  $Z$  ratios, from  $Z = 3.0$  to  $Z = 0$ . The columns of this new matrix correspond to the  $C$  terms.

values, from  $Z = 3$  on the left of the graph up to  $Z = 0$  on the right. Simultaneously, the column-points are ordered also according to axis 1, but in the opposite increasing order, from  $C = 0.2$  on the left up to  $C = 1.2$  on the right of the graph. Each sub-series of row-points corresponding to the same carboxylate ion, with its different  $Z$  values, is stretched all along axis 1.

#### 4.3. Selectivity of eluents

The selectivity of eluents appears when the projection of the row-points is examined through

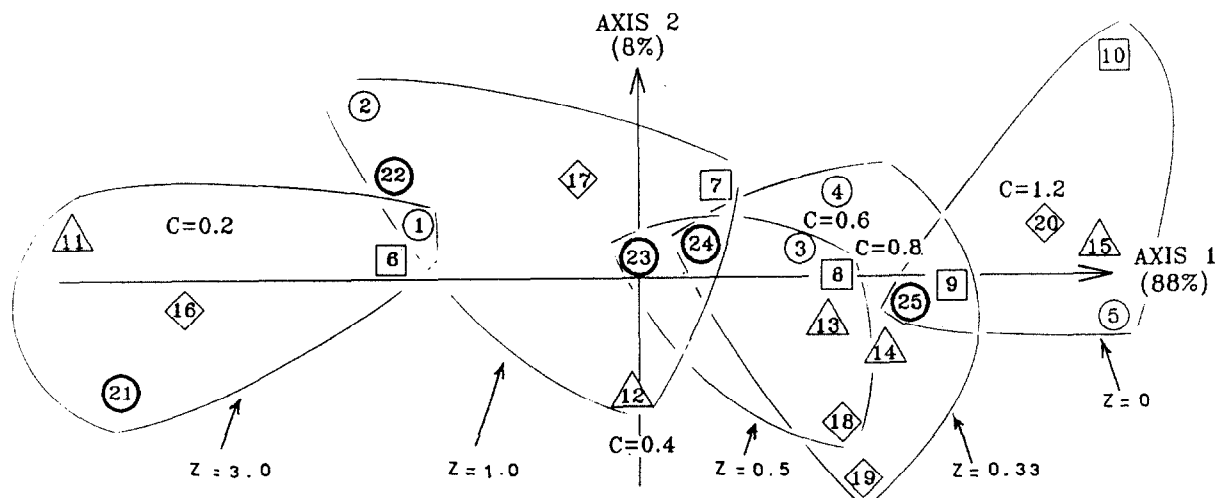


Fig. 2. CFA map of the data matrix where the columns are the concentrations of the eluents ( $C$ ) and the rows are the five carboxylate ions studied with five different  $Z$  values of the ratio of carbonated species. Labels are given in Table 3. Each series of carboxylate ions constitutes  $\text{HCOO}^-$  (○),  $\text{CH}_3\text{COO}^-$  (□),  $\text{C}_2\text{H}_5\text{COO}^-$  (△),  $\text{C}_3\text{H}_7\text{COO}^-$  (◇) and  $\text{C}_4\text{H}_9\text{COO}^-$  (⊙). The clusters delineate the different  $Z$  values. The points inside these clusters correspond to the behaviour of the five anions studied at this  $Z$  value (cf., Table 3).

the projection of the concentration of the eluents.

To explain the specific selectivity of the eluents, we selected two carboxylate ions,  $\text{HCOO}^-$  and  $\text{C}_3\text{H}_7\text{COO}^-$ , and the selectivity was calculated as the ratio of the capacity factors of these two ions. To clarify the projections, we hide all row-points corresponding to the other three carboxylate ions,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_2\text{H}_5\text{COO}^-$  and  $\text{C}_4\text{H}_9\text{COO}^-$ . Then the selectivity between the pairs of points 1–16, 2–17, 3–18, 4–19 and 5–20 corresponding to the values of  $Z = 3.0$ , 1.0, 0.5, 0.33 and 0.0, respectively, at five levels of concentration, are calculated. The results are given Fig. 3. It has been demonstrated [14] that the selectivity can be estimated on CFA maps. The selectivity is measured as the distance between the projection of the row-points considered on the axis defined by a chromatographic system and the origin of the axes. A consequence of this method is that the best chromatographic system, able to separate two compounds, is the one which is projected near the two compounds. This consequence is shown in Fig. 3. For example, points 5 and 20 are separated with the best selectivity, equal to 1.45, when the

concentration of the eluent is high, equal to 1.2. Effectively, both points are projected near the column-point  $C = 1.2$ . In the same manner, the highest selectivities between the points 2–17 and 3–18 are obtained with low concentrations of the eluent,  $C = 0.2$  and 0.4, respectively. These points are projected near column-points  $C = 0.2$  and 0.4, respectively.

With the pairs 1–16 and 4–19, the analysis of the selectivity is more complex. Compounds 1 and 4 are far from compounds 16 and 19. Each pair defines a direction that has two components, one along axis 1 and the other along axis 2. The column-point  $C = 0.4$  projected on axis 2 defines a direction along axis 2. Hence the column-point gives a good selectivity for the separation of the pairs 1–16 and 4–19. The first conclusion is that pair 1–16 is separated with an equal selectivity with eluents projected along axes 1 and 2. Second, for the pair 4–19, the best selectivity is obtained with a concentration of the eluent  $C = 0.4$ . The selectivity is a function of both  $C$  and  $Z$  terms. With a high value of the  $Z$  terms the selectivity is better when the concentration is kept to a low value, and *vice versa*.

The CFA maps (Figs. 2 and 3) give simulta-

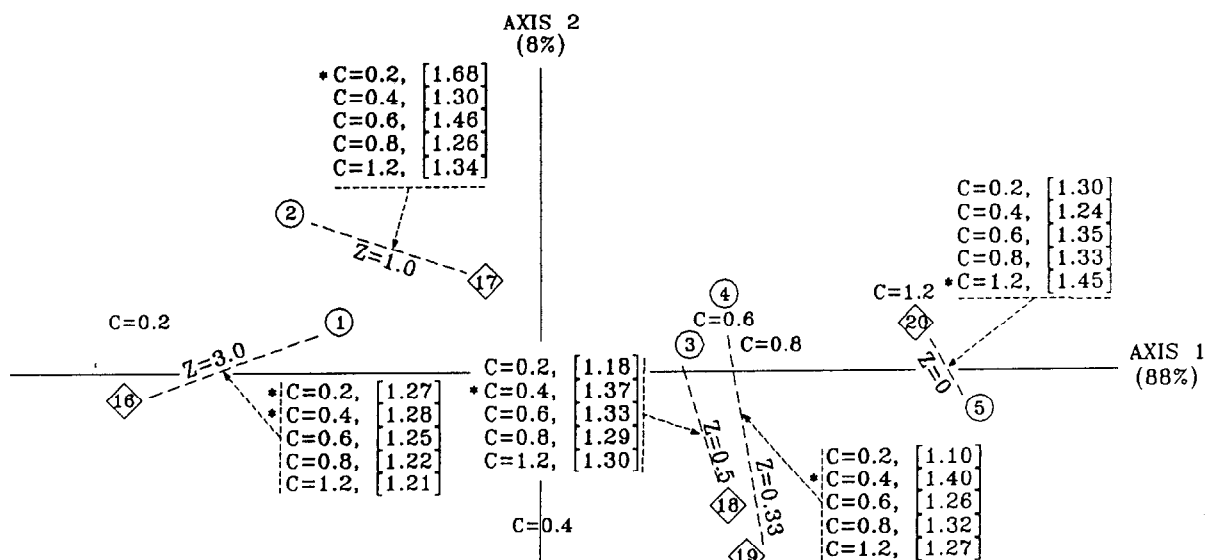


Fig. 3. Partial CFA map used for optimization. The complete CFA map is given in Fig. 2. The carboxylate ions are limited to  $\text{HCOO}^-$  (○) and  $\text{C}_3\text{H}_7\text{COO}^-$  (◇). The projections of the other carboxylate ions are hidden. The values of the selectivity obtained with different values of the concentration of the eluent (C) are given in brackets. The asterisks indicate the C terms that induce the best selectivity.

neous representations of the variation of the retention times and the selectivity *versus* the concentration of the eluent.

## 5. Conclusions

In a general way, factor analysis applied to the study of large matrices of retention data can be a valuable tool for the chromatographer. Evidently, it is only a means of revealing the information content nested in the data matrix. Part of this information content can be evident to a well trained chromatographer. However, the main interest is in offering a quantitative analysis of the information content on a statistical basis. Further, it could be a valuable method to reveal hidden factors that can be important from a mechanistic or optimization point of view.

PCA helps to model the retention times. The fact that only one PCA factor is necessary for calculating the retention time of each carboxylate ion, with its mean retention time, suggests that only one main retention mechanism is responsible for the measured retention times.

This mechanism is most probably an ion-exchange equilibrium.

Keeping this in mind, one should ask why anions with a higher  $n$  value in  $\text{H}(\text{CH}_2)_n\text{COO}^-$  are more retained. It should be noted that all the carboxylic acids studied have pK values in the range 3.75–4.86, *i.e.*, they are all completely ionized in the carbonate eluents applied. If only one main retention mechanism is taking place, it does not mean that it is a simple one. Further, it rules out, with a high probability, the possibility of the anions having a longer aliphatic chain being retained, on the chromatographic column, by a specific mechanism, independent of the main mechanism. The hydrophobic effect of the aliphatic group in the anions studied could certainly be involved [20]. This hydrophobic effect increases with increasing chain length. This “structure-making” effect causes an additional stabilization for the resin-linked anions  $\text{H}(\text{CH}_2)_n\text{COO}^-$  because the resin surface itself is probably also a “structure maker”. The result of such stabilization is an increase in the concentration of resin-linked anions, which in turn leads to longer retention times for the anions

with a more pronounced “fatty” character, *i.e.*, with higher values of  $n$ . The  $\text{HCOO}^-$  ions are not “structure makers” but “structure breakers”; therefore, they are outside a regular evolution of the retention with increasing value of  $n$ .

An analysis of trends of effects acting, at a second-order level, on this main mechanism are delineated by CFA. This method gives a more in-depth data analysis of the experimental data matrix [21]. This analysis shows how the concentrations of carbonate eluents modify, relatively, both the retention times and the selectivity of the chromatographic system. The selectivity is a function of the  $C$  and  $Z$  terms. Even if the mechanism of retention, *i.e.*, the roles of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  and of the alkyl chain on the modification of the selectivity, is explained only qualitatively, such approaches could be useful for optimizing the separation of various mixtures of carboxylate ions by IC.

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