Retention modelling of electrostatic and adsorption effects of aliphatic and aromatic carboxylic acids in ion-exclusion chromatography

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Abstract

The retention mechanism of aliphatic and aromatic carboxylic acids in ion-exclusion chromatography has been investigated with consideration of simultaneous electrostatic repulsion effects and hydrophobic adsorption effects. A mathematical relationship between the retention factor of the analyte and the mobile-phase composition (sulfuric acid concentration and percentage of methanol), the type of analyte (pK_a and hydrophobicity) and some physical characteristics of the stationary phase has been derived. Thirteen carboxylic acids (comprising mono- and divalent, aliphatic and aromatic acids) were chosen and used to acquire retention data on three different cation-exchange stationary phases (in which the sulfonate functional groups are bound to polystyrene–divinylbenzene, polymethacrylate or silica) using 14 mobile-phase compositions of varying pH and percent methanol. These retention data were used to derive the parameters necessary to solve the retention using non-linear regression. In this way, a quantitative measure of the effects of adsorption phenomena on analyte retention were obtained. The model was then used to optimise the separation of nine carboxylic acids. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Retention models; Optimization; Ion-exclusion chromatography; Carboxylic acids

1. Introduction

Ion-exclusion chromatography was first introduced by Wheaton and Bauman in 1953 [1]. The technique involves the separation of partially ionised species on strong anion- or cation-exchange resins. In this mode of chromatography, negatively charged ions are separated on cation-exchange columns, either silica or polymer based, with chemically bound anionic sulfonate or carboxylate functional groups. Positively charged ions (e.g. basic compounds) are separated on anion-exchange columns (silica or a polymer) con-taining cationic quaternary ammonium functional groups. This is the opposite situation to that occurring in ion-exchange chromatography.

In ion-exclusion chromatography, the chromatographic system can be considered to consist of three phases: the eluent phase, the resin phase, and the occluded liquid phase. The eluent passing through the interstitial volume of the column constitutes the mobile phase. The occluded liquid phase is the eluent that is immobilised within the pores of the resin phase, and this trapped liquid acts as the stationary phase of the system. The resin phase is the solid resin network and functionalised groups which can be considered as a semi-permeable ion-exchange membrane separating the flowing mobile phase from

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the stationary occluded liquid inside the resin [2]. Ionic species like strong acids (R^-) are considered to be completely excluded from the interior of the resin by the fixed anionic functional groups, in accordance with the Donnan exclusion effect. Therefore, these species are not retained and pass through the column with the mobile phase front. Partially ionised species, such as weak carboxylic acids (pK_a=2.5–6.5), permeate selectively into the stationary phase (the occluded liquid trapped within the pores of the resin), resulting in some retention of these species, which are then eluted sometime later than the fully ionised solutes.

Due to the many factors which affect retention in ion-exclusion chromatography [2–6], development of a comprehensive mathematical retention model is difficult unless simplifications are made. Glod and Kemula [7] derived a retention model for ion-exclusion chromatography by making the assumption that ionic repulsion exerts the dominant influence on retention, and then later extended this model to provide a more quantitative description of the peak shapes of the eluted analytes [8]. The role of analyte adsorption on the resin phase has been considered by Glod and Stafiej [9], who derived the following equation:

$$D_A = \frac{V_s + K_H V_A}{\left(1 + \dfrac{K_a}{c_b}\right) V_s} \tag{1}$$

where D_A is the distribution coefficient, V_s is the volume of the stationary phase, V_A is the volume of adsorbed layer on one theoretical plate, K_H is Henry's isotherm adsorption constant, and c_b is the mobile phase buffer concentration.

In the present paper we report the results of a comprehensive investigation into influences of electrostatic repulsion and hydrophobic adsorption effects on the retention of a range of aliphatic and aromatic carboxylic acids in ion-exclusion chromatography using three different types of stationary phases. A retention model is presented which provides a quantitative description of adsorption phenomena in ion-exclusion chromatography and this model considers the two main eluent variables, namely $[H^+]$ and percent methanol. This model is then used for optimisation of the eluent composition in ion-exclusion chromatography.

2. Theory

Fig. 1 gives a schematic representation of ion-exclusion chromatography showing the mobile phase (m), the stationary phase (s), and the resin phase (r), together with some of the equilibria involved in ion-exclusion chromatography separations. When a weak acid analyte, HR, is injected onto the column, dissociation proceeds according to:

$$HR_m \rightleftharpoons H_m^+ + R_m^- \quad K_a = \frac{[H^+]_m [R^-]_m}{[HR]_m} \tag{2}$$
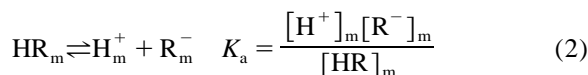
where the subscript m refers to the mobile phase and K_a is the acid dissociation constant of the analyte. The partitioning of the neutral acid between the mobile phase and the stationary phase is described by Eq. (3). Since the mobile and stationary phases are characterised by equal concentrations of the neutral form of the solute, the partition coefficient, K_p, is equal to unity.
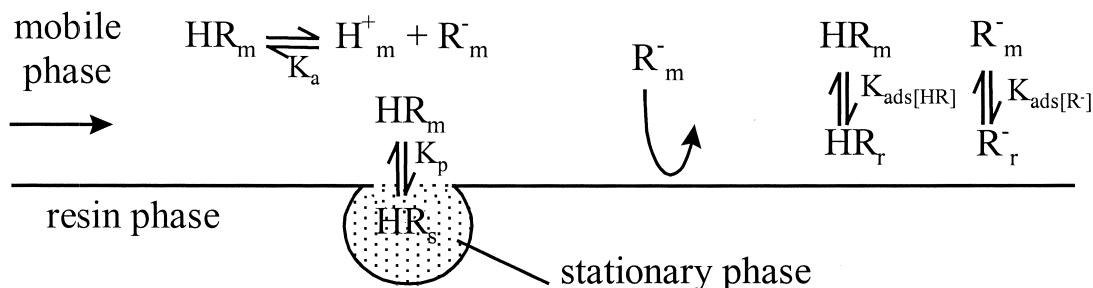

Fig. 1. Schematic showing the four equilibria present in the ion-exclusion chromatography system.

$$HR_m \rightleftharpoons HR_s \quad K_p = \frac{[HR]_s}{[HR]_m} = 1 \tag{3}$$

where the subscript s refers to the stationary phase. The acid anion is negatively charged and is repelled by the anionic sulfonate functional groups on the surface of the resin and so remains in the mobile phase. The neutral acid and its anion can also adsorb onto the uncharged surface of the resin phase according to Eqs. (4) and (5).

$$HR_m \rightleftharpoons HR_r \quad K_{ads[HR]} = \frac{[HR]_r}{[HR]_m} \tag{4}$$

$$R_m^- \rightleftharpoons R_r^- \quad K_{ads[R^-]} = \frac{[R^-]_r}{[R^-]_m} \tag{5}$$

The two adsorption coefficients, $K_{ads[HR]}$ and $K_{ads[R^-]}$, quantify the magnitude of the contribution of adsorption to the retention mechanism of the carboxylic acid.

The retention factor, k' defined in the usual way can, therefore, be represented as:

$$k' = \frac{[HR]_s V_s + [HR]_r V_r + [R^-]_r V_r}{[HR]_m V_m + [R^-]_m V_m} \tag{6}$$

where V_m is the volume of mobile phase (ml), V_s is the volume of stationary phase (ml) and V_r is the volume of resin phase (ml). Dividing the numerator and denominator of Eq. (6) by $[HR]_m$ and recalling Eq. (3), Eq. (2) is substituted into Eq. (6) and becomes:

$$
\begin{aligned}
k' &= \frac{V_s + \dfrac{[HR]_r}{[HR]_m}V_r + \dfrac{[R^-]_r}{[HR]_m}V_r}{V_m + \dfrac{[R^-]_m}{[HR]_m}V_m} \\[2mm]
&= \frac{V_s + K_{ads[HR]}V_r + \dfrac{[R^-]_r}{[HR]_m}V_r}{V_m + \dfrac{K_a}{[H^+]_m}V_m}
\end{aligned}
\tag{7}
$$

From Eq. (5),

$$[R^-]_m = \frac{[R^-]_r}{K_{ads[R^-]}} \tag{8}$$

Combining Eqs. (8) and (2) gives:

$$\frac{[R^-]_r}{[HR]_m} = \frac{K_a K_{ads[R^-]}}{[H^+]_m} \tag{9}$$

Which when substituted into Eq. (7) and combined with Eq. (4) gives:

$$k' = \frac{V_s + \left(K_{ads[HR]} + \dfrac{K_a}{[H^+]_m}K_{ads[R^-]}\right)V_r}{\left(1 + \dfrac{K_a}{[H^+]_m}\right)V_m} \tag{10}$$

The retention factor, k' defined in Eq. (10) is valid only for a purely aqueous mobile phase. In order to take into account the effects of methanol in the mobile phase, the solvophobic equation derived for reversed-phase HPLC must be incorporated. The solvophobic equation is as follows [10]:

$$\ln k' = \ln k_w - s\varphi \tag{11}$$

where k' is the retention factor of the analyte in the aqueous–organic solvent, k_w is the retention factor of the analyte in an aqueous mobile phase, φ is the percent (v/v) of methanol present in mobile phase, and s is a constant which represents the slope of the solvophobic plot. By substituting k' from Eq. (10) into k_w in Eq. (11), Eq. (12) is obtained as the retention model of this system.

$$\ln k' = \ln \frac{V_s + \left(K_{ads[HR]} + \dfrac{K_a}{[H^+]_m}K_{ads[R^-]}\right)V_r}{\left(1 + \dfrac{K_a}{[H^+]_m}\right)V_m} - s\,\varphi \tag{12}$$

3. Experimental

3.1. Instrumentation

The ion chromatograph comprised a Waters Model 6000A pump, Model U6K injector, Model 717 plus autosampler, Model 484 tunable absorbance detector operated at 220 nm and Model TCM temperature control module (Milford, MA, USA). Chromatograms were recorded using a Waters Maxima 820 Chromatographic Workstation. Manual injections

were performed using a 100-μl syringe (Scientific Glass Engineering, Ringwood, Australia).

The ion-exclusion columns used were a Tosoh TSKGel SCX (Tokyo, Japan), 300×7.8 mm I.D. (a 5-μm polystyrene–divinylbenzene (PS–DVB) co-polymer, functionalised with sulfonate groups, capacity 4.2 mequiv./g), a Tosoh TSKGel SP-5PW, 300×7.8 mm I.D. (a 5-μm polymethacrylate co-polymer, functionalised with sulfonate groups, capacity 0.3 mequiv./ml), and a sulfonated silica column, 300×7.8 mm I.D. (packed with 5-μm Develosil silica (Nomura, Japan), laboratory func-tionalised, capacity 0.275 mequiv./g).

Non-linear regression analysis of the retention data was carried out using SigmaPlot for Windows, version 3.03 (Jandel Scientific Software, San Rafael, CA, USA).

3.2. Reagents

The mobile phase consisted of sulfuric acid (Ajax Chemicals, Auburn, Australia) and HPLC-grade methanol (BDH, Poole, UK). Other reagents were of analytical or laboratory grade and were used without further purification. Eluents were prepared in water purified using a Milli-Q water system (Millipore, Bedford, MA, USA), and were filtered and degassed through HPLC 0.45-μm membrane filters before use. Stock solutions of the carboxylic acid solutes were prepared as 10 mM solutions in water and diluted to 1 or 0.1 mM before use.

3.3. Procedures

The experimental space was defined by varying [H$^+$] from 5×10^{-6}–5×10^{-4} M, and percent metha-nol from 0 to 20%, as shown in Fig. 2. The black circles represent eluent conditions used for all the three columns and white squares represent additional eluent conditions used for the TSKGel SCX and TSKGel SP-5PW columns only. In all of the experi-ments, the following chromatographic conditions applied: eluent flow-rate of 1.00 ml/min, column temperature of 35°C, injection volume of 100 μl, and detection using UV absorbance at 220 nm. The columns were conditioned with each mobile phase for at least 36 h each time a new eluent was used. When the eluent contained methanol, a negative
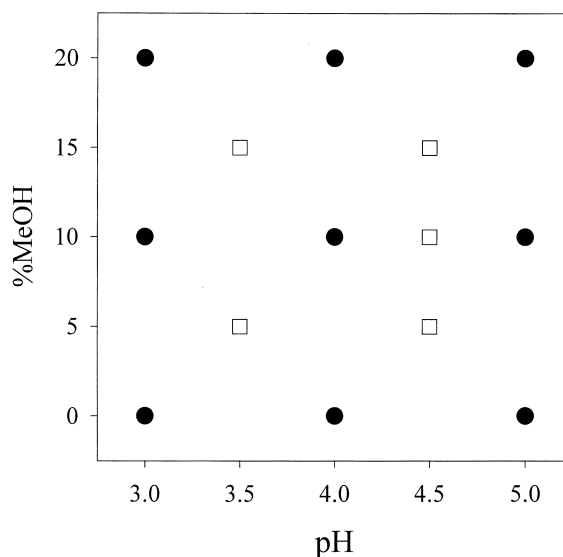

Fig. 2. Experimental area used. (●) Represent eluent conditions used for all three columns; (□) represent eluent conditions used for TSKGel SCX and TSKGel SP-5PW columns only.

system peak was observed at the retention volume of methanol, which obscured the solute peaks eluted near that position. In order to circumvent this, the solute was diluted in the eluent which eliminated the system peak.

Thirteen carboxylic acids were used in this work: formic, acetic, propionic, butyric, valeric, malonic, succinic, glutaric, adipic, citric, benzoic, salicylic and phthalic acids. The experimental data were obtained by taking the average of three replicates for the injection of each solute at each eluent condition.

The void volume of the column (V_m) was de-termined by measuring the retention volume of a 0.1 mM solution of nitric acid. The volume of the occluded liquid phase (V_s), was determined by injecting a 20-μl sample of methanol. Methanol is a small neutral molecule which does not adsorb onto the surface of the resin and, therefore, is free to enter the occluded liquid phase and the retention volume of methanol ($V_R(MeOH)$) is given by Eq. (13).

$$V_R(MeOH) = V_m + V_s \qquad (13)$$

The volume of the resin in the column (V_r) was hence determined by subtracting V_s and V_m from the column volume of 14.335 ml.

4. Results and discussion

4.1. Retention behaviour of the analytes

The relationship between the retention factor and pK_a of the carboxylic acids on the PS–DVB column using a sulfuric acid eluent is shown in Fig. 3. When retention is controlled solely by electrostatic repulsion effects, the retention factor obtained using a constant mobile phase composition should increase as the degree of ionisation decreases (i.e. as pK_a decreases). Such behaviour is evident for monocarboxylic acids and dicarboxylic acids having three or fewer carbon atoms. However, for larger acids the retention factor increased substantially with the number of carbon atoms, even when pK_a showed little change. These results are in agreement with previous studies of the retention mechanism of ion-exclusion chromatography [4,5] and show that for the higher-molecular mass acids, there was a second mechanism contributing to retention. This secondary mechanism has been attributed to hydrophobic adsorption onto the neutral, unfunctionalised regions of the polymeric resin, in a manner similar to that observed in reversed-phase HPLC [5,11]. In the case of aromatic acids, the adsorptive effects are much stronger than for aliphatic acids, presumably due to interaction of π-electrons of the benzene ring of the acid with those of the styrene–divinylbenzene matrix of the ion exchanger [12].

Previous studies have shown that retention of carboxylic acids decreased with increasing pH of the eluent, due to increased ionisation of the analytes [5,6,13–15]. Fig. 4 shows that both mono- and
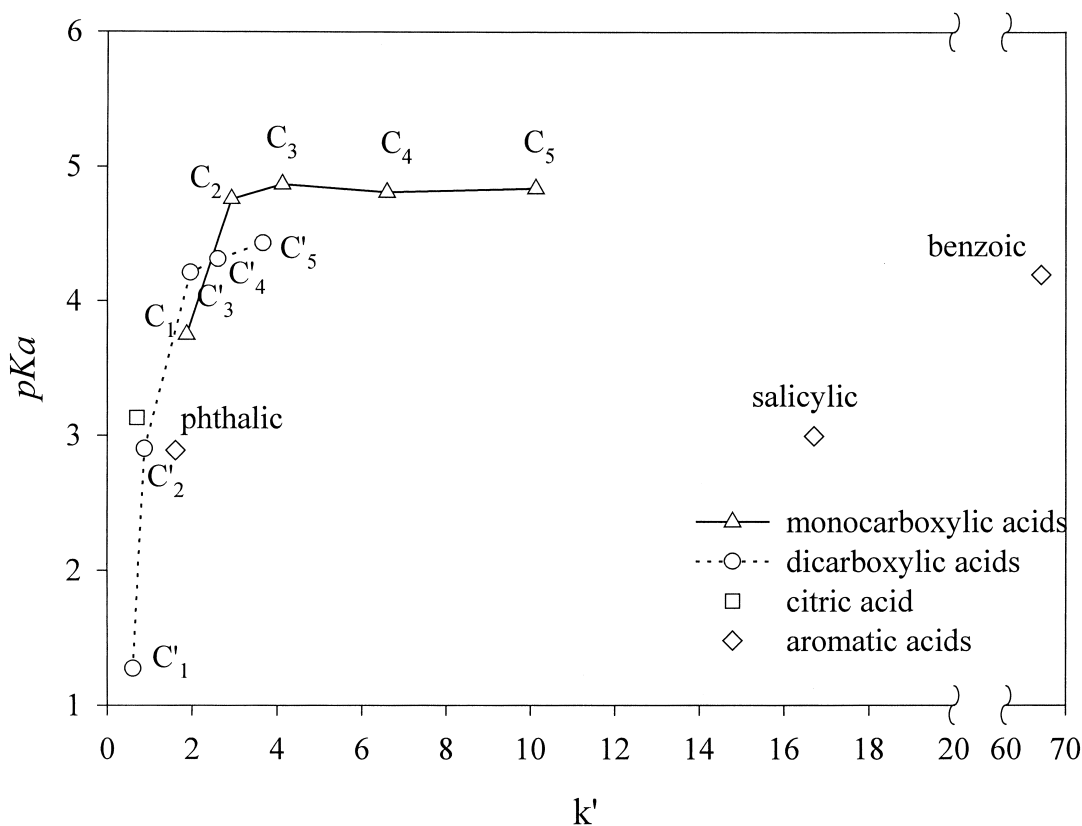

Fig. 3. Relationship between retention factors and pK_a of carboxylic acids on a PS–DVB column using 5×10^{-5} M sulfuric acid (pH 4.02) as the mobile phase for monocarboxylic acids (C_1–C_5), dicarboxylic acids (C'_1–C'_5), citric acid, benzoic acid, salicylic acid and phthalic acid.
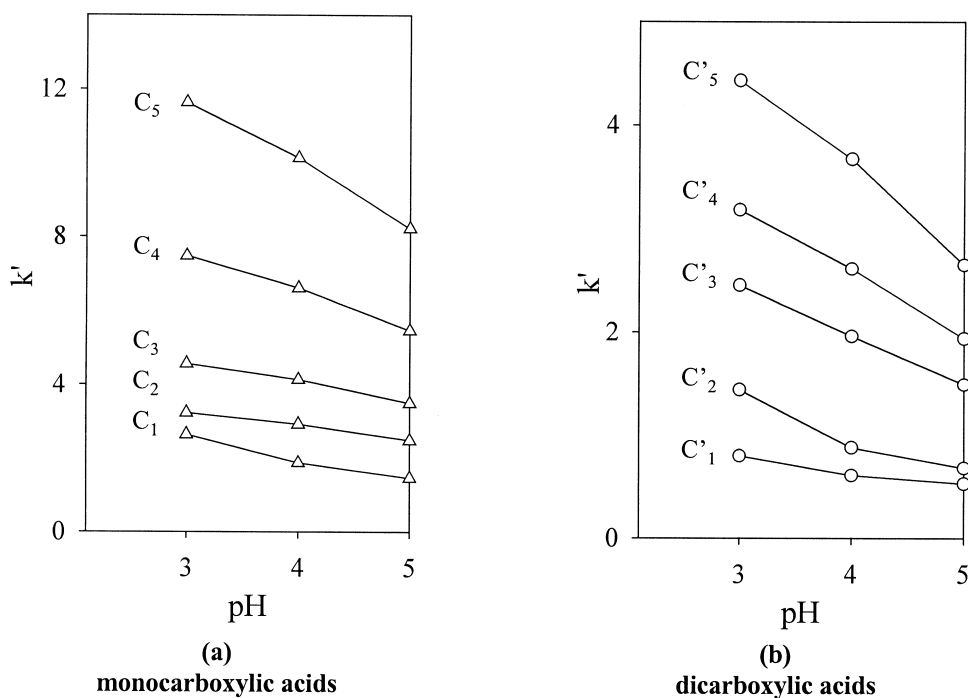
Fig. 4. Relationship between the retention factors of carboxylic acids and the pH of the eluent on the PS–DVB column using sulfuric acid only as the eluent. (a) Monocarboxylic acids, C_1-formic acid to C_5-valeric acid. (b) Dicarboxylic acids, C_1'-oxalic acid to C_5'-adipic acid.

dicarboxylic acids exhibited this behaviour over the pH range 3–5. Fig. 4 also shows that the charge of the analyte anion influences the retention mechanism in that the retention factor of a particular mono-carboxylic acid (C_n) was larger than that for the corresponding dicarboxylic acid (C_n') having the same number of carbon atoms, that is, $k'(C_n) > k'(C_n')$. This behaviour can be anticipated from the additional electrostatic repulsive effects experienced by the analytes with multiple charge. For both mono- and dicarboxylic acids, retention factors increased with increasing chain length of the acid, that is, $k'(C_1) < k'(C_2) < k'(C_3)$ and so on. This can be explained by the fact that the longer-chain acids have a larger hydrophobic region which can adsorb onto the surface of the resin, thereby increasing retention.

It has been demonstrated [6,16,17] that the addition to the mobile phase of typical reversed-phase organic modifiers, such as methanol or acetonitrile, causes a decrease in the retention for some solutes. Fig. 5 shows that for both monocarboxylic acids and aromatic acids, retention factors were found to

decrease with increasing methanol in the mobile phase, provided that the analyte showed appreciable hydrophobic adsorption onto the resin phase. This is the case for monocarboxylic aliphatic acids having three or more carbon atoms and for monocarboxylic aromatic acids. Dicarboxylic acids were relatively unaffected by the addition of methanol to the mobile phase. The effects of methanol can be explained using conventional solvophobic effects used to describe retention behaviour in reversed-phase HPLC [10]. The observed increase in retention factor at higher concentrations of methanol for formic acid can be explained by the fact that the addition of methanol to the eluent causes an increase in the pK_a of the acid [19]. This effect was not observed for aliphatic monocarboxylic acids larger than formic acid because for these analytes, adsorption made a significant contribution to the retention mechanism. Although not shown here, the same effect was observed for the dicarboxylic acids, and similar trends were observed on the polymethacrylate and silica columns.
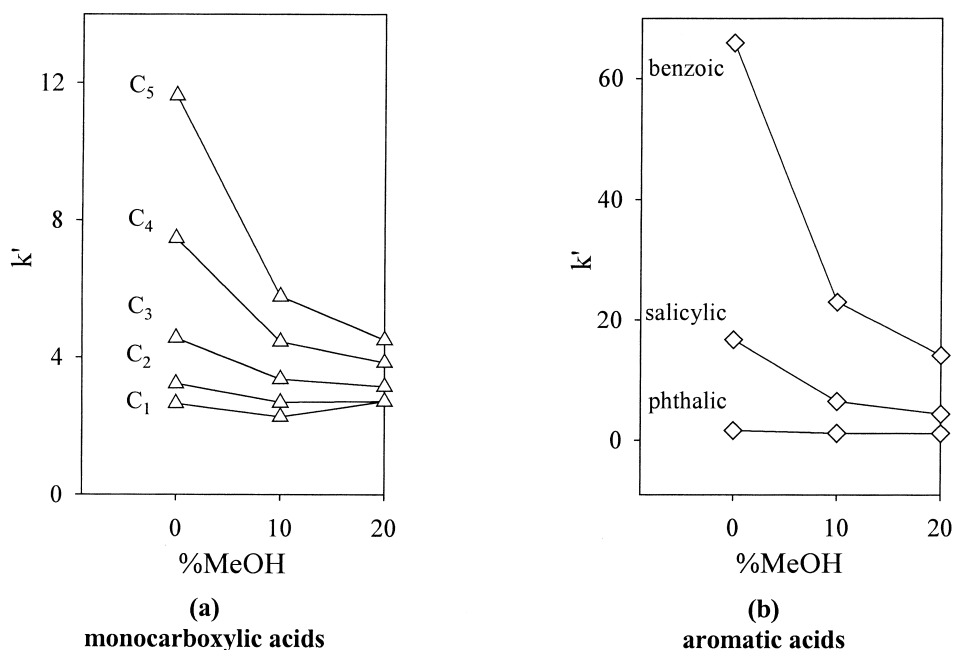
Fig. 5. Relationship between the retention factors of carboxylic acids and the percent (v/v) methanol in the eluent on the PS–DVB column. (a) Monocarboxylic acids, C_1-formic acid to C_5-valeric acid, using a 5×10^{-3} M H_2SO_4–MeOH eluent. (b) Aromatic acids, using a 5×10^{-5} M H_2SO_4–MeOH eluent.

4.2. Application of the retention model

In the retention model (Eq. (12)), the retention factor of an analyte depends on several parameters; namely the K_a value of the solute, $[H^+]$ in the mobile phase, percent methanol, the volumes of the mobile, stationary and resin phases (V_m, V_s and V_r), the adsorption coefficient of the neutral acid molecule ($K_{ads[HR]}$), the adsorption coefficient of the acid anion ($K_{ads[R^-]}$), and s, the value of the slope. These last three parameters are the only unknown variables in the equation and can be calculated by non-linear regression analysis. The experimental values for the retention factors of the carboxylic acids were fitted to Eq. (12) and values of the parameters $K_{ads[HR]}$, $K_{ads[R^-]}$ and s were determined. The retention model equation was then used to predict the retention behaviour of the carboxylic acids. Fig. 6 shows typical predictions of retention behaviour of some of the carboxylic acids over the experimental space.

Fig. 7 shows the correlation between predicted and observed retention factors by plotting $\ln k'$ of the calculated and experimental data from the 13 car-

boxylic acids at 14 different eluent conditions for the two columns, TSKGel SCX and TSKGel SP-5PW as well as for nine eluent conditions for the sulfonated silica column. The three sets of data provided a possible maximum of 481 points, but there were two instances of unobtainable data at the prescribed eluent conditions for a particular carboxylic acid. In considering the values of the retention factor, there is an elution window between $k'=0$ (for fully ionised species) and $k'=2.80$ (for small, neutral analytes such as methanol). Those analytes that are eluted within this window are influenced predominantly by the ion-exclusion effect while those analytes which are eluted later than $k'=2.80$ are retained also by adsorption effects.

When considering only analytes which are eluted before $k'=2.80$ ($n=330$), the correlation coefficient, r^2, calculated by least-squares regression, is 0.945. For those analytes which are eluted after $k'=2.80$ ($n=149$), $r^2=0.978$. When all the data are combined ($n=479$), the correlation coefficient, r^2, is 0.9755 (Fig. 7). The value of the correlation coefficient provides a high confidence level for using the
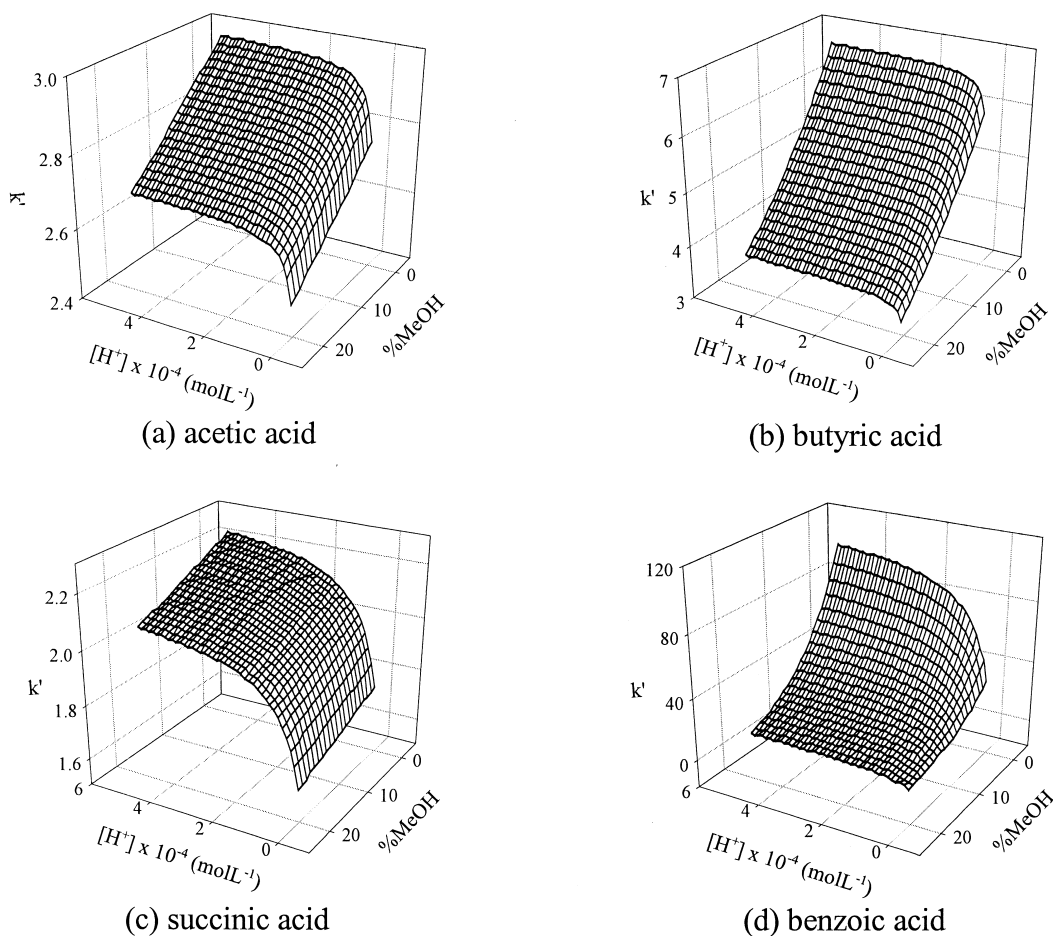
(a) acetic acid

(b) butyric acid

(c) succinic acid

(d) benzoic acid

Fig. 6. Predicted retention factor (k') responses of carboxylic acids on TSKGel SCX column as a function of percent methanol and concentration of acid eluent.

retention equation to model the contribution of adsorption as a mechanism in ion-exclusion chromatography, characterised by the values of the parameters $K_{ads[HR]}$, $K_{ads[R^-]}$ and s.

Table 1 lists the estimated values for the parameters $K_{ads[HR]}$, $K_{ads[R^-]}$ and s for each analyte on each of the three columns. The values of the adsorption coefficients were in general accordance with the expected hydrophobicity of the analytes in that values increased as the chain length of the acid increased, were larger for the monocarboxylic acids than for the corresponding dicarboxylic acid, and were very high for aromatic acids. In terms of the effects of different stationary phase substrates, the adsorption coefficients were generally highest on the

polymethacrylate resin, followed by the PS–DVB resin and were lowest on silica. This agreed with previous studies of the contribution of adsorption to the retention mechanism of carboxylic acids on different substrates [19].

4.3. Selection of optimal separation conditions

The retention model can be used for the prediction of the retention behaviour of analytes on one of the columns using an eluent containing sulfuric acid and methanol, and hence for mobile phase optimisation. Fig. 8 shows the predicted response of the normalised resolution product, r, over the experimental space for the separation of nine carboxylic acids on
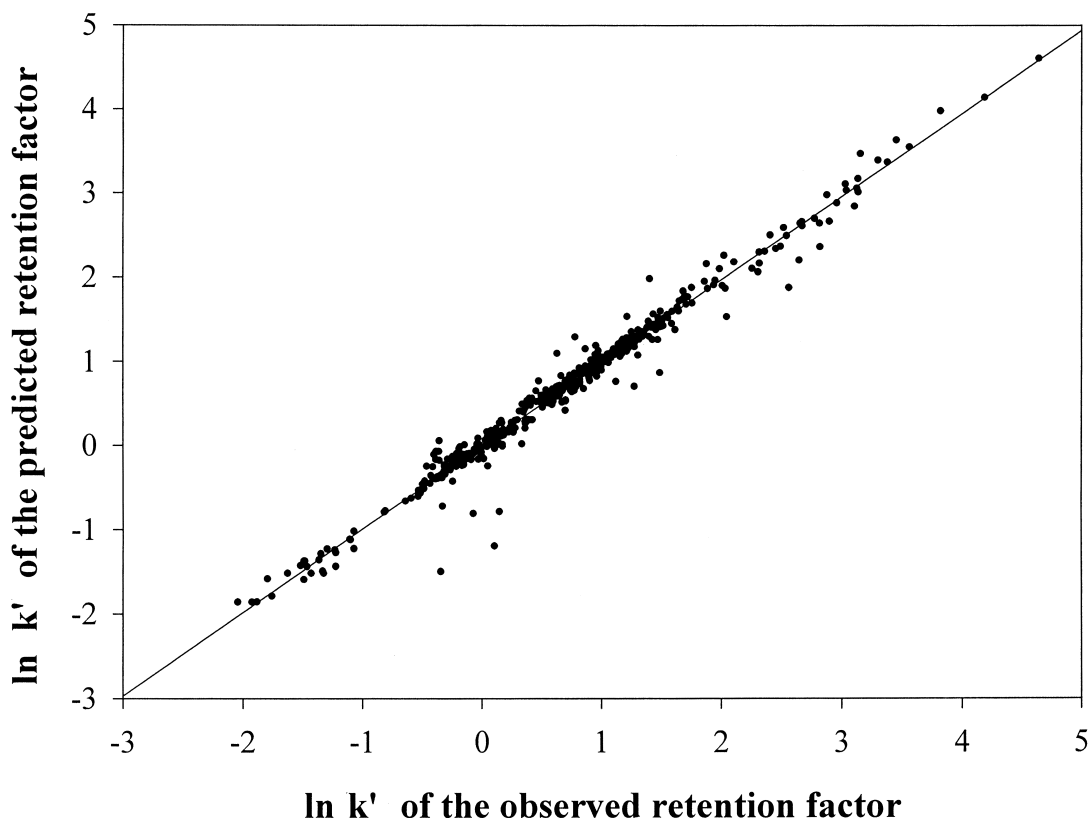
Fig. 7. Plot of the predicted and observed ln k' for 13 carboxylic acids at 14 eluent conditions for TSKGel SCX and TSKGel SP-5PW columns and for 13 carboxylic acids at nine eluent conditions for the sulfonated silica column. The correlation coefficient (r^2) calculated by least-squares regression is 0.9755, slope=0.9886, intercept=-0.005, and n=479.

Table 1
Estimated parameters from fitting the retention model based on the data at 14 different eluent conditions for the TSKGel SCX, TSKGel SP-5W and the sulfonated silica column

| Acid	TSKGel SCX			TSKGel SP-5PW			Sulfonated silica		
	$K_{ads[HR]}$	$K_{ads[R^-]}$	s	$K_{ads[HR]}$	$K_{ads[R^-]}$	s	$K_{ads[HR]}$	$K_{ads[R^-]}$	s
Formic	<0.1	1.7	<0.1	<0.1	6.7	0.0	<0.1	2.1	<0.1
Acetic	<0.1	2.7	0.5	<0.1	9.1	0.2	<0.1	3.3	0.4
Propionic	0.4	3.7	1.4	0.6	11.1	0.4	<0.1	4.8	1.5
Butyric	2.9	5.7	3.0	4.6	13.8	1.0	1.7	6.3	2.9
Valeric	6.7	8.3	4.6	10.6	17.5	1.7	3.1	7.7	3.7
Malonic	<0.1	1.5	0.0	3.9	4.0	<0.1	<0.1	0.8	<0.1
Succinic	<0.1	1.7	0.4	<0.1	7.3	0.1	<0.1	2.1	<0.1
Glutaric	<0.1	2.2	1.1	0.4	8.1	0.3	<0.1	2.4	<0.1
Adipic	0.4	2.9	2.1	2.1	9.7	0.7	<0.1	2.8	0.2
Citric	<0.1	0.8	<0.1	1.2	3.5	<0.1	<0.1	0.7	<0.1
Benzoic	106	24.7	10.9	121	28.6	3.9	4.0	3.7	3.6
Salicylic	161	6.5	6.9	406	10.5	4.5	4.2	0.9	2.1
Phthalic	29.7	0.9	7.7	46.8	3.5	1.4	1.5	0.5	<0.1
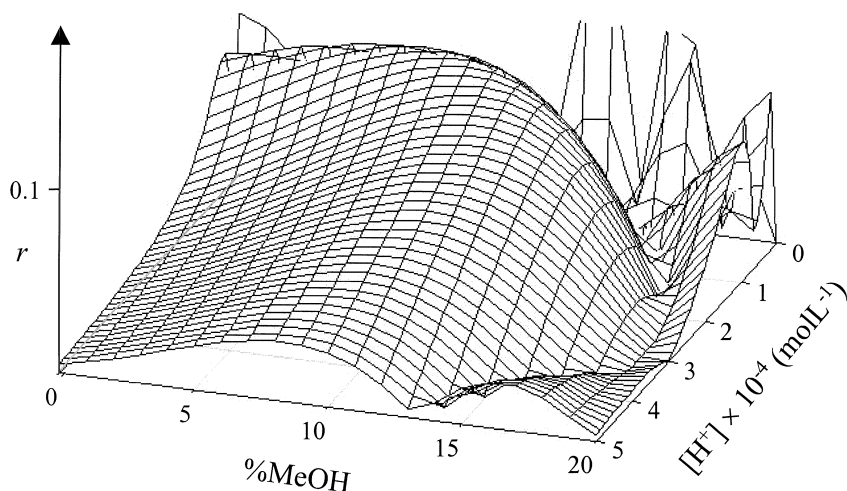
Fig. 8. Response surface showing the normalised resolution product, r, as a function of percent methanol and concentration of acid eluent over the experimental space for the separation of nine carboxylic acids on the TSKGel SCX column. The optimum separation conditions are 12% methanol and $[H^+] = 1.2 \times 10^{-4}$ M with $r = 0.1$.

the TSKGel SCX column. The resolution product, r, is calculated according to:

$$r = \prod_{i=1}^{n-1} \left(\frac{R_{s(i,i+1)}}{\dfrac{1}{n-1} \displaystyle\sum_{i=1}^{n-1} R_{s(i,i+1)}} \right) \qquad (14)$$

where $R_{s(i,i+1)}$ is the resolution for the adjacent peaks i and $i+1$ and is calculated from k' according to Ref. [18]. This criterion reaches its maximum value of 1 when all R_s values are equal, that is, when all peaks are distributed evenly over the chromatogram [19]. The minimum value of zero represents overlapping peaks in the chromatogram. The optimum mobile phase composition is given by the highest value of the criterion over the experimental space. As indicated by Fig. 8, the mobile phase composition predicted for optimum separation is 12% methanol and 1.2×10^{-4} M H_2SO_4. At these conditions, the value of the normalised resolution product, r, is about 0.1. Fig. 9 shows the predicted and observed separation of the carboxylic acids at those eluent conditions, from which it can be seen that generally good agreement was obtained. In the optimal separation, all of the nine carboxylic acids are resolved, except for acetic and adipic acids. At the predicted optimum from the measured chromatogram, the normalised resolution product, $r = 0.16$.
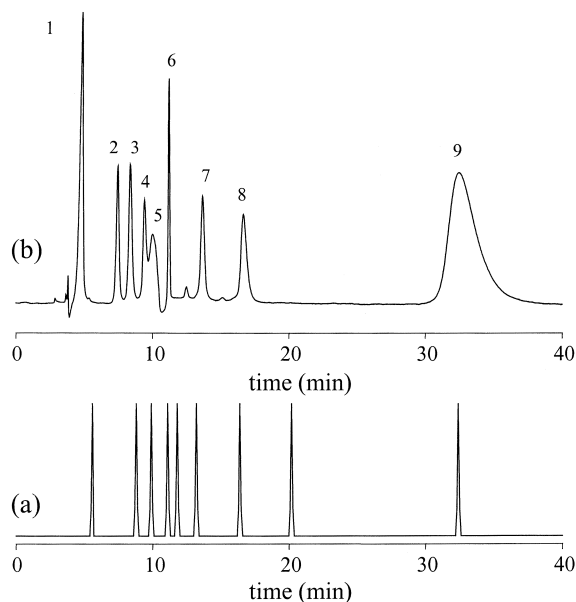

Fig. 9. Chromatogram showing (a) predicted and (b) observed separation of nine carboxylic acids on TSKGel SCX column. Chromatographic conditions: eluent, 1.20×10^{-4} M H_2SO_4 with 12% methanol; flow-rate, 1.00 ml/min; injection volume, 100 µl; detection, 220 nm; temperature, 35°C; concentration of solutes, (1) 1 M citric acid, (2) 1 M succinic acid, (3) 1 M glutaric acid, (4) 1 M acetic acid, (5) 1 M adipic acid, (6) 1 M propionic acid, (7) 1 M butyric acid, (8) 1 M valeric acid, (9) 0.04 M salicylic acid.

5. Conclusions

A retention model for ion-exclusion chromatography has been derived in which retention factor is expressed as a function of mobile phase composition (concentration and organic modifier content), analyte characteristics (K_a) and adsorption of the analyte to the stationary phase substrate. The model has permitted the degree of adsorption of a particular analyte on a particular column to be expressed quantitatively as an adsorption coefficient for both the neutral and ionised analytes. These values show that hydrophobic adsorption plays a major role in the ion-exclusion chromatography separation of aliphatic monocarboxylic acids that have three or more carbon atoms, and also for aromatic carboxylic acids. Hydrophobic adsorption effects were greatest for a methacrylate-based cation exchanger and least for a silica-based exchanger. The retention model has been shown to be suitable for the prediction of retention behaviour of carboxylic acids in ion-exclusion chromatography and also for the selection of optimal mobile phase composition.

Acknowledgements

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