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Nonlinear function retention model in weak acid anion chromatography

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Abstract

A nonlinear function retention model for anion chromatography is developed, which is able to predict the retention behavior of polyvalent weak acid anions using sodium hydroxide as eluent. The relationship between the retention factors of phosphate and resorcinol and eluent concentration was studied with sodium hydroxide as the eluent. Both retention factors of the analyte anions first increase then decrease with the increase of sodium hydroxide concentration. The estimated values agree with the measured values with correlation coefficients for phosphate and resorcinol of 0.9920 and 0.9916, respectively, which shows the nonlinear function model is a useful addition to the theory of anion chromatography. The model is able to optimize the separation of polyvalent weak acid anions. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ion chromatography is an effective method for the separation and determination of cations and anions. In weak anion chromatography, the retention behavior of an analyte is governed mainly by the eluent concentration. The pH value and thus acid–base equilibria play an important role too [1]. For the analysis of monoanionic species, when using an eluent containing only one kind of anion which does not participate in any side equilibria such as dissociation/protonation, the dependence of the analyte retention on the eluent concentration is a straight line with a slope given by the ratio of charges of analyte and eluting ions [2]. If an ion chromatography

system contains a polyanionic eluent and/or polyanionic analytes, the analyte anions or eluent anions may be present in several states having different charges with the pH change, which complicates the retention behavior. The analyte retention depends on the pH values as well as the eluent concentration and the relationship between the retention factor and eluent concentration cannot be transformed to a simple liner log–log form. Maki and Danielson [3] studied the retention of inorganic ions with different naphthalenesulfonic acids as eluents. The results show that the slopes of the experimental straight lines for the polyvalent anion analytes are all greater than expected.

Several models describing the anion analyte retention behavior in ion chromatography (IC) have been developed. Janoš [1] reviewed the retention models in ion chromatography, which emphasize on

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the side equilibria in ion chromatography of inorganic cations and anions. Madden and Haddad [4,5] made a systematic comparison of seven theoretical retention models for predicting the retention factors of inorganic anions in non-suppressed IC (using phthalate eluents on three different stationary phases) and in suppressed IC (using carbonate–hydrogencarbonate eluents on a Dionex AS4A stationary phase). The models include the linear solvent strength model (using both the dominant equilibrium approach and the competing ion effective approach) [6–8], Hoover model [9], dual eluent species model [10–12], Kuwamoto model [13], extended dual eluent species model [14], multiple species eluent/analyte model [15] and empirical end points model [4]. Their study shows that the performance of the theoretical models improved with the complexity of the model whereas none of the theoretical models could give sufficiently reliable prediction of retention factors for the model to be used in optimization software. However, the empirical end-points model gave the most satisfactory performance. Madden et al. [16] also compared the retention models in anion chromatography using hydroxide eluents on a Dionex AS11 stationary phase and pointed out that DryLab gave the best accuracy and precision of the three models investigated.

In this work, a nonlinear function model is developed to predict the retention behavior of polyvalent weak acid anions using a monoanionic anion as eluent. The effect of the eluent concentration on the retention factors of phosphate and resorcinol was studied using sodium hydroxide as eluent. The curve obtained from experiment was compared with that from our model.

2. Theory

If the analytes are strong acid anions which contain only monoanionic species while using monoanionic eluents in anion chromatography, the dependence of a logarithm of the retention factor on the logarithm of the concentration of the eluent is given by the following equation [1]:

$$\log k = \text{const} - (y/x) \log C \quad (1)$$

where y is the charge of the analyte ion, x is the charge of the eluent ion, const is a constant that depends on the column, eluent and analyte ion. For the analytes of polyvalent weak acid anions, the anion coexists in more than one ionized form. In weak acid anion chromatography, if the absolute value of the highest charge of the weak acid anion is defined as m , there are m kinds of ionized existing forms of the weak acid in the eluent. The fraction of species of each existing form is a function of the pH of the eluent.

We defined av as the average charge of the weak acid analyte anions:

$$\text{av} = \sum_{i=1}^m \alpha_i i \quad (2)$$

where α_i is the fraction of species of anion that carries i negative charges.

In our study sodium hydroxide is used as eluent and the pH value of the eluent is above 11. As shown in Fig. 1, the analyte anions (phosphate and resorcinol) mostly exist in the highest charge and secondary high charge forms in the eluent. The retention behavior of weak acid anions is controlled mainly by the retention of the analyte anions with the

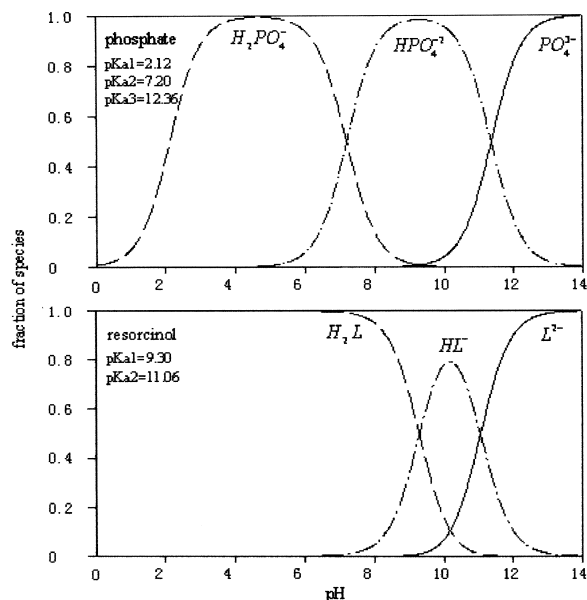


Fig. 1. Fraction of species for phosphate and resorcinol.

highest charge and the secondary high charge, therefore the fraction of species of the analyte anions with highest charge and secondary high charge controls the retention behavior of polyvalent weak acid analyte anions.

According to the above discussion, we present the following function to establish the dependence of the retention factors of weak acid anions change with the concentration of monoanionic eluent such as sodium hydroxide derived from Eq. (1):

$$\log k = a \sum_{i=1}^m \alpha_i \log C + b_1 \log \alpha_h + b_2 \log \alpha_{sh} + d \quad (3)$$

where α_h is the fraction of species of anions with highest charge, α_{sh} is the fraction of species of anions with secondary high charge, a , b_1 , b_2 , d are the constants that depend on the column, eluent and analyte.

If the absolute value of the highest charge of analyte is 2:

$$\alpha_h = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_{sh} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

where $[H^+]$ is the function of concentration of the eluent, it indicates that the fraction of species of the analyte is also a function of the eluent concentration.

3. Experimental

A Dionex Model 2010 ion chromatograph was equipped with an AG4A guard column (5 cm × 4 mm I.D.), an AS4A separation column (25 cm × 4 mm I.D.), an anion micromembrane suppressor (AMMS), a conductivity detector and an ultraviolet detector. The AMMS was continuously regenerated with 0.0125 M sulfuric acid. A Pentium II personal computer was used for data processing.

Sodium hydroxide, sodium carbonate stock eluent solutions (100 mmol/l) were prepared by dissolving special-reagents in deionized water, diluted to appropriate volume and deaerated by ultrasonic vibration. The sodium carbonate concentration in all eluents

was 3 mmol/l. The mobile phase flow-rate was 1.5 ml/min. The migration time of the solvent (deionized water) peak was regarded as the void time and was 1.34 min.

Standard 1000 mg/l sample solutions were prepared by dissolving resorcinol, sodium phosphate in deionized water. All standard sample solutions were prepared from analytical-reagent grade reagents. Standard working solutions of 10 mg/l were obtained by diluting the stock solution with the eluent solution.

4. Results and discussion

Although phosphoric acid ($pK_{a1}=2.12$) is not a weak acid, HPO_4^{2-} ($pK_{a2}=7.20$) and $H_2PO_4^-$ ($pK_{a3}=12.36$) are very weak acids. Adding sodium carbonate to the eluents in our experiment increased the elution power of the eluent and therefore can shorten the analysis time. As the concentration of sodium carbonate is constant and the existing forms of sodium carbonate are mostly divalent anions in the pH range of our experiment, the effects of sodium carbonate on retention factor of weak acid anions can be merged into the constant. Resorcinol ($pK_{a1}=9.30$, $pK_{a2}=11.06$) is a very weak organic acid, which can partially dissociate into mono- and divalent anions. Since its acidity is too weak to detect using conductivity detection, ultraviolet detection at 254 nm was used in our experiment.

The effect of the eluent concentration of sodium hydroxide on the retention factors of phosphate and resorcinol is shown in Table 1 and Table 2. The retention factors of phosphate and resorcinol are clearly increasing instead of decreasing as sodium hydroxide concentration increases firstly. But as sodium hydroxide concentration further increases in the eluent, the speed of retention factors increase becomes more and more slow. The retention factors clearly decrease finally. This is because along with increasing concentration of sodium hydroxide, the fractions of species of high valence anions increase. The higher proportion of highly-charged ions increases the retention factor. But along with sodium hydroxide concentration further increasing, the speed of fractions of species of high valence anions increase becomes more and more slow (Fig. 2), the

Table 1
Effects of concentration of sodium hydroxide on retention factors of phosphate

C_{NaOH} (mmol/l)	Log C_{NaOH}	pH	Average charge	α_{h}	Log α_{h}	α_{sh}	Log α_{sh}	k	RSD (%, $n=5$)	Log k
1.0	0.000	11.142	2.057	0.0571	-1.224	0.943	-0.0256	3.58	1.62	0.554
2.5	0.398	11.431	2.105	0.105	-0.978	0.895	-0.0484	3.93	1.43	0.594
4.0	0.602	11.616	2.153	0.153	-0.816	0.847	-0.0720	4.87	1.23	0.688
5.0	0.699	11.708	2.182	0.182	-0.739	0.818	-0.0874	5.14	1.38	0.711
6.0	0.778	11.785	2.210	0.210	-0.678	0.790	-0.102	5.57	0.87	0.746
7.0	0.845	11.850	2.236	0.236	-0.627	0.764	-0.117	5.86	0.82	0.768
8.0	0.903	11.907	2.260	0.260	-0.584	0.740	-0.131	5.64	0.98	0.751
9.0	0.954	11.957	2.283	0.283	-0.548	0.717	-0.148	5.20	0.85	0.716
10.0	1.00	12.002	2.305	0.305	-0.516	0.695	-0.158	4.78	1.33	0.679
11.0	1.041	12.043	2.325	0.325	-0.488	0.675	-0.171	4.69	1.27	0.671
12.5	1.097	12.098	2.354	0.354	-0.451	0.646	-0.190	4.22	1.63	0.625
15.0	1.176	12.177	2.396	0.396	-0.402	0.604	-0.219	3.45	2.04	0.538
17.5	1.243	12.244	2.434	0.434	-0.363	0.566	-0.247	2.86	2.32	0.456
20.0	1.301	12.302	2.466	0.446	-0.331	0.534	-0.273	2.57	2.66	0.410

increase in elution power becomes the main affecting factor and retention factors reduce gradually.

Eq. (3) is used to set up the relationship between the retention factors of weak acid anions and the concentration of the eluent. Given this problem, an answer belongs to the complex unitary non-linear fitting problem. Since it is very difficult to obtain the answer directly, here we transform it to the multiple linear fitting to give the answer.

Let $x_1 = \text{av log } C$ (where av is average charges), $x_2 = \text{log } \alpha_{\text{h}}$, $x_3 = \text{log } \alpha_{\text{sh}}$, $y = \text{log } k$.

From Eq. (3):

$$y = ax_1 + b_1x_2 + b_2x_3 + d \quad (4)$$

A Delphi computer program was designed to deal with the related data by ternary linear regression process and to predict the retention factors of weak acid anions. The results are shown in Table 3, Fig. 3 and Fig. 4.

Fig. 3 and Fig. 4 show the comparison of calculated and measured retention factors of phosphate and resorcinol. The measured and calculated values agree well with the correction coefficient over 0.99.

In the range of sodium hydroxide eluent con-

Table 2
Effects of concentration of sodium hydroxide on retention factors of resorcinol

C_{NaOH} (mmol/l)	Log C_{NaOH}	pH	Average charge	α_{h}	Log α_{h}	α_{sh}	Log α_{sh}	k	RSD (%, $n=5$)	Log k
1.0	0.00	11.142	1.537	0.543	-0.265	0.450	-0.347	3.25	1.27	0.512
2.5	0.398	11.431	1.698	0.670	-0.155	0.298	-0.526	4.30	1.16	0.633
4.0	0.602	11.616	1.781	0.782	-0.107	0.217	-0.664	4.78	1.42	0.680
5.0	0.699	11.708	1.815	0.816	-0.0884	0.184	-0.736	4.89	0.87	0.689
6.0	0.778	11.785	1.840	0.841	-0.0753	0.159	-0.799	4.95	0.76	0.695
7.0	0.854	11.850	1.860	0.860	-0.0655	0.140	-0.855	4.55	0.84	0.658
8.0	0.903	11.907	1.875	0.875	-0.0579	0.125	-0.903	4.32	0.69	0.635
9.0	0.954	11.957	1.887	0.887	-0.0519	0.113	-0.949	4.12	0.83	0.615
10.0	1.00	12.002	1.897	0.897	-0.0471	0.103	-0.987	3.70	1.34	0.568
11.0	1.041	12.043	1.906	0.906	-0.0430	0.0941	-1.0263	3.47	1.71	0.540
12.5	1.097	12.098	1.916	0.916	-0.0381	0.0839	-1.0762	3.33	1.49	0.522
15.0	1.176	12.177	1.929	0.929	-0.0320	0.0709	-1.149	3.00	2.15	0.477
17.5	1.243	12.244	1.938	0.939	-0.0276	0.0615	-1.211	2.75	2.70	0.439
20.0	1.301	12.302	1.946	0.946	-0.0242	0.0542	-1.266	2.58	2.12	0.411

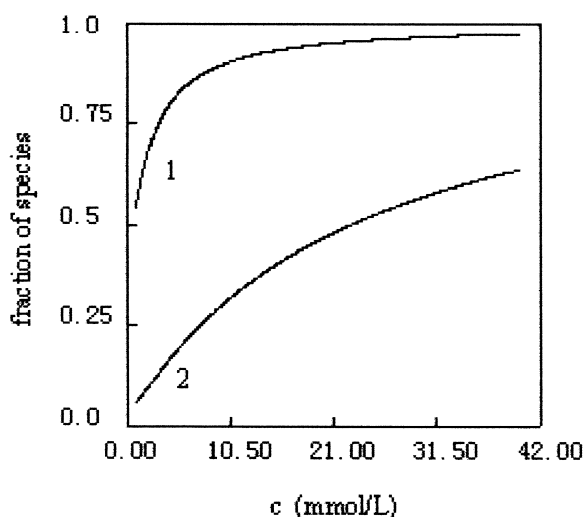


Fig. 2. Dependence of fraction of species on concentration of sodium hydroxide eluents. 1=Resorcinol (–2), 2=phosphate (–3).

centration in common use, the average charge of analyte changes little. The average charge of phosphate goes from -2.057 to -2.466 if the concentration of sodium hydroxide changes from 1 to 20 mmol/l (Table 1). Neglecting the effect of change of average charge, Eq. (3) is reduced to:

$$\log k = a \log C + b_1 \log \alpha_h + b_2 \log \alpha_{sh} + d \quad (5)$$

The correlation coefficient reduces from 0.9920 to 0.9910.

The fractions of species of the highest valence strong acid anions are close to 1, their logarithms equal 0, so Eq. (3) or Eq. (5) is the same with strong acid anions. Since the pK_a values of most unitary weak acids are less than 10, if the sodium hydroxide concentration range is 1–40 mmol/l, as shown in Fig. 5, the fractions of species of most unitary weak acid anions are close to 1, so Eq. (1) is applicable for most unitary weak acid anions.

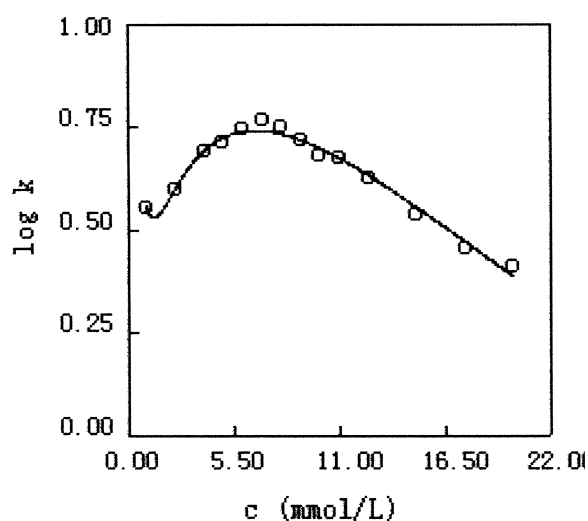


Fig. 3. Calculated dependence logarithms of retention factors of phosphate on concentration of sodium hydroxide together with experimental data (points). Column: AS4A.

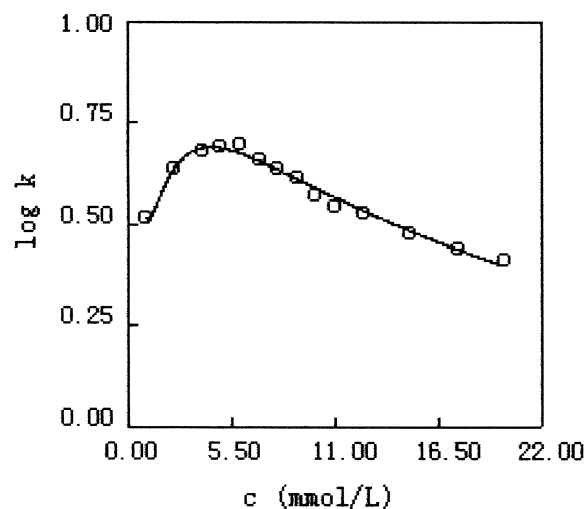


Fig. 4. Calculated dependence logarithms of retention factors of resorcinol on concentration of sodium hydroxide together with experimental data (points). Column: AS4A.

Table 3

Regression equations of logarithms of retention factors and concentration of sodium hydroxide

Analyte	Regression equation	Correlation coefficient
Phosphate	$\log k = -1.242av \log C + 4.108 \log \delta_3 - 0.6029 \log \delta_2 + 4.108$	0.9920
Resorcinol	$\log k = -2.666av \log C + 10.010 \log \delta_2 - 4.594 \log \delta_1 + 1.570$	0.9916

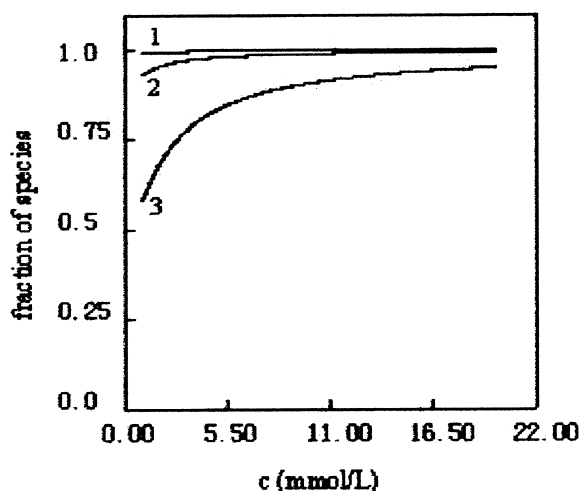


Fig. 5. Dependence of fraction of species of unitary weak acid on concentration of sodium hydroxide. 1, $pK_a=9$; 2, $pK_a=10$; 3, $pK_a=11$.

5. Conclusion

This non-linear function retention model in weak acid anion chromatography was used for predicting the retention values of polyvalent weak acid anions using sodium hydroxide as eluents, which can be used to optimize the separation of polyvalent weak acid anions from other anions. It was used to predict the retention behavior of weak acid anions using

sodium hydroxide as eluent. The estimated values agreed with the measured values, which show our model is a useful addition for the theory of anion chromatography where the application of the usual single-level equation would fail.

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