Journal of Chromatography, 481 (1989) 315–322
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 773

ION CHROMATOGRAPHIC ELUTION BEHAVIOUR AND PREDICTION OF THE RETENTION OF INORGANIC MONOVALENT ANIONS USING A PHOSPHATE ELUENT

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(First received April 10th, 1989; revised manuscript received July 6th, 1989)

SUMMARY

For the prediction of the retention times of inorganic anions with a phosphate eluent, Jenke's model was modified by using the elution system coefficients as a new concept instead of the calculated selectivity coefficients and measured effective column capacity as in Jenke's method. The capacity factors of analytes were precisely determined by using the modified calculation equation over a wide range of pH.

INTRODUCTION

Ion chromatography has been rapidly developed as an analytical method for inorganic and some organic anions and theoretical considerations have been also reported on the separation process, which is based on the partition of an analyte between the eluent and the ion-exchange resin[1–4]. For example, Gjerde *et al.*[5] and Haddad and Cowie[6] found theoretically the capacity factor of an analyte under a fixed charge ratio of analyte anion to eluent anion and fixed concentration of the eluent.

On the other hand, Hoover[7] interpreted theoretically the chromatographic retention data for phosphate and arsenate as a function of pH in carbonate–hydrogencarbonate eluents. Four premises were proposed, as follows: (1) the reduced retention volume of the analyte is equal to the volumetric distribution of the analyte; (2) the effective column capacity is expressed by the sum of adsorbed eluent anions; (3) electroneutrality is maintained during the elution process; and (4) for every pair of ionic species in the system, there is a constant selectivity coefficient corresponding to the concentration equilibrium for the exchange reaction. Moreover, Jenke and Pagenkopf[8,9] studied the retention behaviour of inorganic anions with phthalate eluents by using Hoover's model and obtained the selectivity coefficients by substituting the effective column capacity and experimental retention time into a modified equation. The reduced retention volume was calculated by using above-mentioned coefficients. In addition, a comparison of calculated with experimental retention times was carried out. However, it was difficult to obtain the same values of the effective exchange column capacity, because the measurements could not

0021-9673/89/$03.50

be performed under the same conditions. Accordingly, the selectivity coefficients were not correctly obtained.

On the basis of the above, we investigated the method for the prediction of the retention times of analyte anions with a phosphate eluent by using a modified Hoover equation, in which the empirically calculated elution system coefficients are used. It was found that the modified equation is useful for establishing the possibility of the separation of sample anions.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of a Tosoh CCPD double plunger pump, a Rheodyne 7520 injection valve (sample injection volume 1 μl), a Shimadzu SPD-6AV UV detector (cell volume 0.6 μl) and a stainless-steel microbore column (120 mm × 0.5 mm I.D.) packed with Tosoh TSKgel IC-Anion-PW (particle size 10 μm, exchange capacity 30 μequiv./ml bed). The eluent flow-rate was 20 μl/min.

Eluents and standard solutions

Phosphoric acid (1 *M*), sodium dihydrogenphosphate and sodium hydroxide stock eluent solutions were prepared by dissolving special-grade reagents in deionized, distilled water, diluting to the appropriate volume and deaerating at a water-jet pump and by ultrasonic vibration.

Standard 1000 ppm (as each anion) sample solutions were prepared by dissolving sodium nitrate, sodium nitrite [$pK_a = 3.14$ (ref. 10)], sodium bromide, sodium bromate and sodium selenite [$pK_{a_1} = 2.64$, $pK_{a_2} = 8.26$ (ref. 10)] in distilled, deionized water. All solutions were prepared from analytical-reagent grade salts. Working standard solutions were obtained by diluting the stock solutions with the phosphate eluent.

RESULTS AND DISCUSSION

Theory; modification of Hoover's equations

According to Hoover's premises, the following equilibria should hold on the ion-exchange resin with a phosphate eluent [$pK_{a_1} = 2.10$, $pK_{a_2} = 7.20$, $pK_{a_3} = 12.38$ (ref. 10)] in the pH range 4.7–9.6:

$$K_1 = [\text{R–S}][\text{H}_2\text{P}^-]/[\text{R–H}_2\text{P}][\text{S}^-] \tag{1}$$

$$K_2 = [\text{R–S}]^2[\text{HP}^{2-}]/[\text{R}_2\text{–HP}][\text{S}^-]^2 \tag{2}$$

where K_1 and K_2 denote the ion-exchange equilibria constants between the monovalent phosphate anion (H_2P^-) and sample anion (S^-) and between the divalent anion (HP^{2-}) and the sample anion on the ion exchange resin (R).

The exchange capacity of an ion-exchange resin is expressed as follows:

$$\text{Cap} = [\text{R–H}_2\text{P}] + 2[\text{R}_2\text{–HP}] + [\text{R–S}] \tag{3}$$

where Cap denotes the ion-exchange capacity and [R–S] is neglected because the concentration of the analyte is very small. Substitution of eqns. 1 and 2 into eqn. 3 provides

$$\mathrm{Cap} = [\mathrm{H_2P^-}][\mathrm{R{-}S}]/K_1[\mathrm{S^-}] + 2[\mathrm{HP^{2-}}][\mathrm{R{-}S}]^2/K_2[\mathrm{S^-}]^2 \tag{4}$$

The capacity factor (k') of an analyte anion and the total concentration ($[P_\mathrm{T}]$) of the eluent are expressed by

$$k' = q[\mathrm{R{-}S}]/[\mathrm{S^-}] \tag{5}$$

$$[P_\mathrm{T}] = [\mathrm{H_2P^-}] + [\mathrm{HP^{2-}}] \tag{6}$$

where q is the phase ratio.

The dissociation constant, K_{a_2}, of the phosphate eluent is expressed as a function of $[\mathrm{H^+}]$ by

$$K_{\mathrm{a}_2} = [\mathrm{H^+}][\mathrm{HP^{2-}}]/[\mathrm{H_2P^-}] \tag{7}$$

Substitution of eqns. 5, 6 and 7 into eqn. 4 provides

$$[P_\mathrm{T}]^{-1} = [1/(K_1 q\mathrm{Cap})]\{[\mathrm{H^+}]/(K_{\mathrm{a}_2} + [\mathrm{H^+}])\}k' + {} + [2/(K_2 q^2\mathrm{Cap})]\{K_{\mathrm{a}_2}/(K_{\mathrm{a}_2} + [\mathrm{H^+}])\}k'^2 \tag{8}$$

By use of the elution system coefficients $[C_1 = 1/(K_1 q\mathrm{Cap})$ and $C_2 = 2/(K_2 q^2\mathrm{Cap})]$,

$$[P_\mathrm{T}]^{-1} = C_1\{[\mathrm{H^+}]/(K_{\mathrm{a}_2} + [\mathrm{H^+}])\}k' + C_2\{K_{\mathrm{a}_2}/(K_{\mathrm{a}_2} + [\mathrm{H^+}])\}k'^2 \tag{9}$$

At a given pH value,

$$[P_\mathrm{T}]^{-1} = C_1'k' + C_2'k'^2 \tag{10}$$

If the charge number of analyte anion is n,

$$[P_\mathrm{T}]^{-1} = C_1''k'^{1/n} + C_2''k'^{2/n} \tag{11}$$

As a result, if $[P_\mathrm{T}]$, K_{a_2} and the pH of the eluent are fixed, C_1' and C_2' can be determined empirically by using the observed k', which is a measurable value under the defined conditions.

Concentration of phosphate eluent

Fig. 1 shows the dependence of the concentration of the phosphate eluent on the capacity factor of the nitrate anion. Although the relationship between the concentration of the eluent and the capacity factor is estimated to be nearly linear at pH 5.20 of the eluent ($[\mathrm{H_2P^-}]$:$[\mathrm{HP^{2-}}]$ = 99:1) because the dominant species in the eluent is monovalent phosphate, the observed relationship was curved, as shown in the figure. Moreover, although the slope of plots of log k' *versus* $-\log[P_\mathrm{T}]$ represents the ratio of

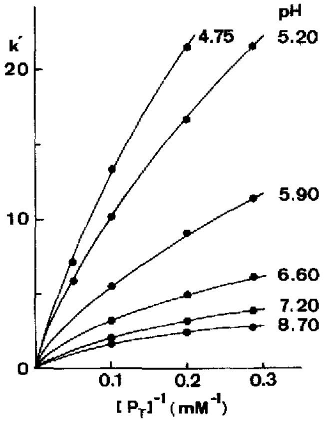

Fig. 1. Dependence of the capacity factor of nitrate on the concentration of phosphate eluent.

the charge of the sample anion to that of the eluent anion (according to Gjerde *et al.*[5]), the measured value at pH 5.20 was 0.71 compared with the calculated value of 0.99. At pH 7.20, the measured value of the slope was 0.46 compared with the calculated value of 0.67. These facts show that the divalent phosphate anion is very strongly retained in the column compared with the monovalent phosphate anion. Therefore, even if the ratio of the concentration of divalent phosphate anion to that of total phosphate in the eluent is small, the influence of the divalent anion on the retention time of the sample anion cannot be neglected because the measured value of the slope was smaller than the calculated value. The relationship between k' and $[P_T]^{-1}$ on the other anions was almost the same as that of nitrate ion.

pH of phosphate eluent

Fig. 2 shows the dependence of the pH of the phosphate eluent on the capacity factors of analyte anions. The capacity factors of the analytes decreased rapidly with increasing pH in the pH range studied, in which the divalent to monovalent

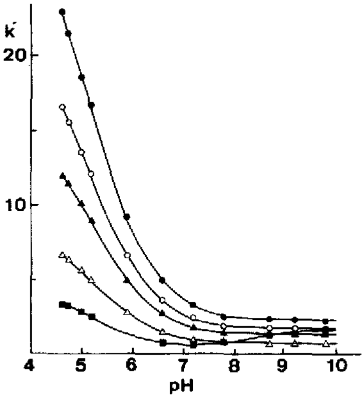

Fig. 2. Dependence of the capacity factor on the pH of the eluent. Sample: (●) nitrate; (○) bromide; (▲) nitrite; (△) bromate; (■) selenite. Eluent: 5 m*M* phosphate.

concentration ratio of phosphate anions is very small, and the intensified elution power is maintained above pH 7, where the monovalent anion is converted into the divalent anion.

Calculation of the elution coefficients C_1 and C_2

To calculate C_2 in eqn. 9, the simultaneous equations were solved by selecting two different pH values (A, B) of the eluent. The C_2 values obtained are given in Table I. As can be seen, if pH(B) is 8.70 or 9.20, C_2 of nitrate is 0.038 regardless of pH(A) in the range 4.75–9.20. At pH(B) 9.60, the C_2 values become large. This may be caused by the influence of trivalent phosphate formed at increasing pH. Finally, C_2 values were obtained easily at pH 8.70–9.20, because the elution power of the monovalent phosphate anion is very weak at high pH and the first term of eqn. 9 can be neglected.

C_1 values obtained by solving simultaneous equations were influenced considerable, especially at high pH. Accordingly, C_1 had to be determined at low pH in order to make the second term of eqn. 9 as small as possible. In practice, C_1 values were obtained by substituting the C_2 value at pH 8.70 into eqn. 9. The results are given in Table II. From these results, it was concluded that a pH of the eluent lower than 5.00 is to be preferred (the pH of the eluent is 2.2 smaller than the pK_{a_2} value of phosphate).

From eqn. 9, the following relationship between C_1 and C_2 is obtained: $C_1 = 1/(K_1 q\text{Cap})$ and $C_2 = 2/(K_2 q^2 \text{Cap})$ from eqn. 9;

$$\begin{aligned} C_1^2/C_2 &= \tfrac{1}{2}(K_2/K_1^2)(1/\text{Cap}) \\ &= \tfrac{1}{2}([\text{R–H}_2\text{P}]^2[\text{HP}^{2-}]/[\text{R}_2\text{–HP}][\text{H}_2\text{P}^-]^2)(1/\text{Cap}) \\ &= \text{constant} \end{aligned} \tag{12}$$

where K_2/K_1^2 is the selectivity coefficient between monovalent and divalent phosphate anions on the ion-exchange resin, which is the same as the term K_E in Jenke's

TABLE I

C_2 VALUES (l/mmol) OBTAINED BY SOLVING THE SIMULTANEOUS EQUATIONS

Sample: nitrate; P_T = 5 m*M*.

pH (A)	*pH (B)*						
	4.75	*5.20*	*6.60*	*7.20*	*8.70*	*9.20*	*9.60*
4.75	–	0.029	0.036	0.036	0.038	0.038	0.041
5.20		–	0.036	0.036	0.038	0.038	0.041
6.60			–	0.036	0.038	0.038	0.041
7.20				–	0.038	0.038	0.042
8.70					0.038[a]	0.038	0.042
9.20						0.038[a]	0.044
9.60							0.041[a]

[a] Determined by neglecting the first term in eqn. 9.

TABLE II

C_1 VALUES (l/mmol) OBTAINED BY USING C_2

$P_T = 5$ m*M*.

pH	*Sample*			
	NO_3^- *($C_2 = 0.038$)*	*Br^-* *($C_2 = 0.072$)*	*NO_2^-* *($C_2 = 0.13$)*	*BrO_3^-* *($C_2 = 0.41$)*
4.62	0.0065	0.0090	0.012	0.022
4.75	0.0065	0.0090	0.012	0.023
5.00	0.0064	0.0087	0.012	0.021
Av. (pH = 4.62–5.00)	0.0065	0.0089	0.012	0.022
5.20	0.0057	0.0078	0.011	0.020
5.90	0.0059	0.0081	0.011	0.020
6.60	0.0042	0.0038	0.008	0.024

TABLE III

C_1, C_2 AND C_1^2/C_2 FOR EACH SAMPLE

Sample	*C_1* *(l/mmol)*	*C_2* *(l/mmol)*	*C_1^2/C_2* *(l/mmol)*
NO_3^-	0.0065	0.038	0.0011
Br^-	0.0089	0.072	0.0011
NO_2^-	0.012	0.13	0.0011
BrO_3^-	0.022	0.41	0.0012
$HSeO_3^-$	0.049	0.93[a]	0.0026

[a] C_2 value of selenite was determined at pH 7.20.

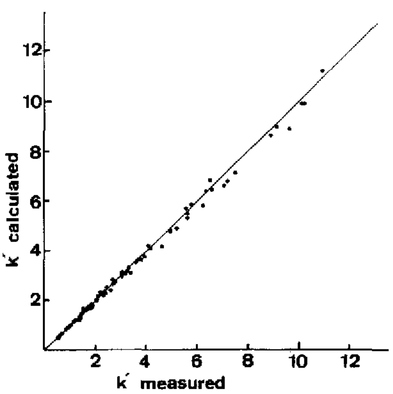

Fig. 3. Comparison of measured and calculated capacity factors by eqn. 9. $k'_{\text{calc.s}}$ of each sample (nitrate, bromide, nitrite and bromate) was calculated by using C_1 and C_2 as shown in Table III. The pH used is one of 4.62, 4.75, 5.00, 5.20, 5.90, 6.60, 7.20, 7.80, 8.70, 9.20 and 9.60, and the eluent concentration is one of 3.5, 5, 10 and 20 m*M*. $k'_{\text{meas.s}}$ values were measured under the same conditions as $k'_{\text{calc.s}}$.

equation[9]. C_1^2/C_2 values are obtained by using above-mentioned C_1 and C_2 values. The results are given in Table III. As can be seen, the C_1^2/C_2 values for each sample were approximately the same, except for that of selenite. The C_1 and C_2 values of selenite were not obtained accurately, because the charge number of selenite varies under acidic and basic conditions. As mentioned above, if the total concentration and the pH of the eluent are fixed under the same chromatographic conditions, k' can be evaluated by using the elution system coefficients C_1 and C_2.

In the calculation of k', the C_2 value obtained at pH 8.70 and the average value of C_1 obtained at pH below 5.00 were used. Fig. 3 shows the comparison of calculated and measured capacity factors. The measured and calculated values agree well in the pH range 4.62–9.60; the average relative error is 2.5%

It is concluded that, if C_1 and C_2 are determined experimentally, k' for analytes over a wide range of pH and concentrations of the eluent can be precisely predicted.

Chromatograms

On the basis of the above results, the separation of nitrate, bromide, nitrite, bromate and selenite was undertaken by using the conditions 5 m*M* phosphate eluent, pH 5.20 and flow-rate 20 µl/min. The chromatograms obtained are shown in Fig. 4.

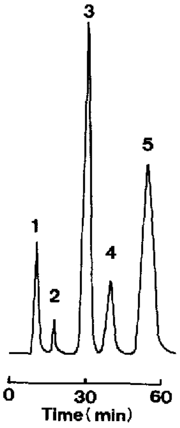

Fig. 4. Chromatograms of inorganic anions. Sample: 1 = selenite; 2 = bromate; 3 = nitrite; 4 = bromide; 5 = nitrate. Eluent: 5 m*M* phosphate (pH 5.20). Wavelength: 210 nm. Flow-rate: 20 µl/min.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support from the Nippon Life Insurance Foundation.

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