

Short Communication

Application of ion chromatography to the determination of selectivity coefficients

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ABSTRACT

Ion chromatography was applied to calculate the selectivity coefficients between Cl^- , NO_3^- , HPO_4^{2-} and SO_4^{2-} ions on HIKS-1 resin containing $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ groups. For each combination of ions, 25 different eluents were applied.

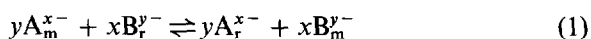
INTRODUCTION

Ion chromatography is based on the assumption that the retention times (t_R) of the ions present in the sample are virtually independent of their concentration [1,2]. On the other hand, retention times depend on several factors, including the type of resin in the separation column [3]. Provided that an ion chromatogram has been obtained isocratically, the selectivity coefficients between the sample ions on the resin used can be determined. Further, by changing the eluent in the next run it is possible to examine the influence of eluents on the selectivity coefficients obtained. Selectivity coefficients may be considered to be dependent on the resin used as a whole. Nevertheless, it is to be expected that selectivity coefficients will depend greatly on the type of functional groups of the resin.

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THEORETICAL

The ion-exchange equilibrium for the binding of two solute anions, A^{x-} and B^{y-} , to a stationary phase in a separation column is given by



where the subscripts m and r refer to the mobile and stationary phase, respectively. Neglecting the activity coefficients, the selectivity coefficient for the system is given by [4]

$$K_{A,B} = \frac{[\text{A}_r^{x-}]^y [\text{B}_m^{y-}]^x}{[\text{A}_m^{x-}]^y [\text{B}_r^{y-}]^x} = \frac{D_A^y}{D_B^x} \quad (2)$$

The distribution coefficients $D_A = [\text{A}_r^{x-}]/[\text{A}_m^{x-}]$ and $D_B = [\text{B}_r^{y-}]/[\text{B}_m^{y-}]$ are related to the retention times $t_{R,A}$ and $t_{R,B}$ respectively. In general [5,6],

$$D = (t_R - t_0)/pt_0 \quad (3)$$

where p is the phase ratio ($p = V_r/V_m$; V_r and V_m are the volumes of resin and mobile phase in the separation column) and t_0 is the void time [7] of the separation column. If a chemical suppressor is used, the retention time t_R also includes the retention time

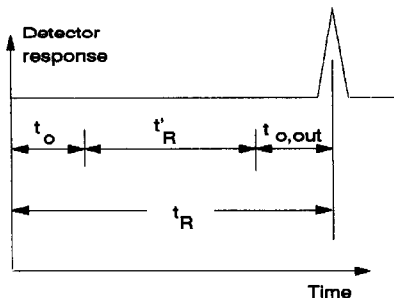


Fig. 1. Parameters for defining retention: t_R = retention time measured for the whole system; t'_R = reduced retention time for the separation column; t_0 = void time for the separation column; $t_{0,out}$ = the time due to the mobile phase outside the separation column.

$t_{0,out}$ due to the mobile phase outside the separation column (in the tubing used to interconnect the chromatographic components, in the suppressor device, etc.). The parameters t_0 , t_R and $t_{0,out}$ are illustrated in Fig. 1. In a good chromatographic system $t_{0,out} \ll t_0$. However, if a classical suppression column is involved, $t_{0,out}$ and t_0 may be of the same order of magnitude. In this respect the use of single-column ion chromatography [8] is to be preferred, because usually in this instance $t_{0,out} \ll t_0$. Taking the time $t_{0,out}$ also into account, eqn. 3 can be rewritten as

$$D = (t_R - t_{0,out} - t_0)/pt_0 \quad (4)$$

Provided that the retention times $t_{R,A}$ and $t_{R,B}$ used in eqn. 4 for calculating D_A and D_B , respectively, were obtained from the same chromatogram, $t_{0,out}$ is the same for both the ions A^{x-} and B^{y-} . Substitution of D_A and D_B (eqn. 4) into eqn. 2 gives

$$K_{A,B} = \frac{(t_{R,A} - t_{0,out} - t_0)^y}{(t_{R,B} - t_{0,out} - t_0)^x} (pt_0)^{x-y} \quad (5)$$

If the two solutes, A^{x-} and B^{y-} have equal charge numbers, $x = y = 1$, then eqn. 5 reduces to

$$K_{A,B} = (t_{R,A} - t_{0,out} - t_0)/(t_{R,B} - t_{0,out} - t_0) \quad (6)$$

EXPERIMENTAL

We calculated the selectivity coefficients (eqn. 5) between Cl^- , NO_3^- , HPO_4^{2-} and SO_4^{2-} ions by making use of the corresponding retention times (t_R) given in ref. 9, where values are available for 25 different carbonate eluents for each ion considered.

The retention times in ref. 9 were measured on a Model IVK-1 ion chromatograph (Design Office of the Estonian Academy of Sciences, Tallinn, Estonia) equipped with a JD-1 conductimetric detector. The separation column (200 × 3 mm I.D.) was packed with HIKS-1 resin (Himifil Co, Tallinn, Estonia) and the suppression column (250 × 4 mm I.D.) with KU-2 resin (Sojuzkhimreaktiv, Moscow, Russia). Ion exchange on the HIKS-1 resin occurred on the $-CH_2N(CH_3)_3$ groups. The capacity of the HIKS-1 resin was 0.022 mequiv./cm³.

The sum $t_0 + t_{0,out}$ was measured by injecting doubly distilled water instead of a sample containing the ions studied, and $t_{0,out}$ was measured in the same way on the same equipment but with the suppression column only (i.e., with the separation column removed). The void time t_0 was calculated as the difference $(t_0 + t_{0,out}) - t_{0,out}$. We obtained $t_0 = 43$ s and $t_{0,out} = 55$ s by applying the eluent flow-rate used in ref. 9 (1.50 ml/min).

The phase ratio $P = V_r/V_m$ was obtained by taking $V_r = 1.41$ cm³ for the separation column and V_m equal to the weight of water (grams) present in the packed separation column. The latter quantity was determined as the difference between the weight of the wet resin, pressed out from the separation column used, and the weight of the same amount of the resin after drying at 110°C. The phase ratio in the separation column was 1.10.

RESULTS

Using the t_R values from ref. 9, $t_0 = 43$ s and $t_{0,out} = 55$ s, the selectivity coefficients $K_{A,B}$ (eqn. 5) were calculated (see Table I). Each selectivity coeffi-

TABLE I
SELECTIVITY COEFFICIENTS, $K_{A,B}$

$K_{A,B}$	Obtained with eqn. 5, ±S.D. (n = 25)	Calculated from $K_{A,CO_3^{2-}}$ and $K_{B,CO_3^{2-}}$
K_{Cl^-,NO_3^-}	0.39 ± 0.06	0.33
$K_{Cl^-,HPO_4^{2-}}$	0.44 ± 0.13	0.29
$K_{Cl^-,SO_4^{2-}}$	0.21 ± 0.07	0.17
$K_{NO_3^-,HPO_4^{2-}}$	2.88 ± 0.77	2.65
$K_{NO_3^-,SO_4^{2-}}$	1.38 ± 0.41	1.56
$K_{HPO_4^{2-},SO_4^{2-}}$	0.25 ± 0.10	0.35

cient value given is the mean of 25 values obtained for different carbonate eluents [9]. The root mean square errors given in Table I are those with 24 degrees of freedom. The relatively large root mean square errors are probably due mainly to random experimental errors in $t_{R,A}$ and $t_{R,B}$, because no clear dependence of $K_{A,B}$ values on the eluent composition has been found. It should also be noted that eqn. 5, containing the squares of differences if $y = 2$, is sensitive to errors in $t_{R,A}$ and $t_{R,B}$. The $K_{A,B}$ values (eqn. 5) may be compared with those obtained as the ratio of $K_{A,CO_3^{2-}}$ to $K_{B,CO_3^{2-}}$ published elsewhere [10]. The $K_{A,B}$ values obtained in this way are close to those calculated with eqn. 5 (see Table I). It should be pointed out that the $K_{A,CO_3^{2-}}$ and $K_{B,CO_3^{2-}}$ values used were obtained by non-linear regression analysis [10]. The closeness of the $K_{A,B}$ values obtained in this work (with eqn. 5) and by the non-linear regression may be considered mutually to verify the two methods applied.

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