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Carbonate eluents in ion chromatography

Fractions of resin capacity linked to anions present in the eluent

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ABSTRACT

The eluting ions OH^-, HCO_3^- and CO_3^{2-} in carbonate eluents are absorbed on the resin in the separation column. In an equilibrium state, the concentrations of these ions on the resin depend on the composition of the carbonate eluent used. A method for determining the concentrations of the OH^-, HCO_3^- and CO_3^{2-} absorbed on the stationary phase is suggested and an example of its application to HIKS-1 resin is presented.

INTRODUCTION

Since its introduction in 1975 [1], ion chromatography (IC) has become the dominant analytical method for determining a number of anions. Often these analyses are performed with conductimetric detection. To obtain the lowest detection limits possible for the sample anions studied, suppressed IC is applied. This technique requires that the eluent used should have a sufficient eluting efficiency in the separation column, and in the suppressor it should be easily convertible into a weak acid solution with a very low conductivity. Carbonate eluents, aqueous solutions of sodium carbonate and sodium hydrogencarbonate, which have been widely used in IC since its introduction [2], meet these requirements fairly well. The composition of carbonate eluents, *viz.*, the concentrations of Na_2CO_3 and $NaHCO_3$, may be varied over a wide range depending on the sample to be analysed and the capacity of the separation column used. The Na_2CO_3 and $NaHCO_3$ solutions elute the sample anions by a cooperative effect of the three species present in these eluents (OH^-, HCO_3^- and CO_3^{2-}).

A study [3] of ion-exchange equilibria between the carbonate eluents and anion-exchange resins in the separation column did no yield quantitative results. In order to obtain a deeper insight into the ion-exchange processes taking place in the separation column, it seemed to be useful to determine the percentages of the total capacity of the separation column bonded to each of the eluting anions (OH^-, HCO_3^-, CO_3^{2-}). It should be noted that the fraction of the column capacity occupied by the sample anions is usually negligibly small. Hence we can write

$$\bar{C}_{OH^-} + \bar{C}_{HCO_3^-} + 2\bar{C}_{CO_3^{2-}} = Q \qquad (1)$$

where Q is the capacity of the ion-exchange resin in the separation column (mmol/cm^3) and the $\bar{C}$ terms are the concentrations of the respective ions sorbed on the resin (mmol/cm^3). The quantities to be calculated are $F_{OH^-} = \bar{C}_{OH^-} Q^{-1}$, $F_{HCO_3^-} = \bar{C}_{HCO_3^-} Q^{-1}$ and $F_{CO_3^{2-}} = \bar{C}_{CO_3^{2-}} Q^{-1}$.

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METHOD

Neglecting the activity coefficients, the $\bar{C}$ terms in eqn. 1 are given by

$$\bar{C}_{\mathrm{A}} = (K_{\mathrm{A}}^{\mathrm{B}})^{-1/y} D^{x/y} C_{\mathrm{A}} \qquad (2)$$

where $K_{\mathrm{A}}^{\mathrm{B}}$ and $D_{\mathrm{B}} = \bar{C}_{\mathrm{B}}/C_{\mathrm{B}}$ are the ion-exchange constant and partition coefficient, respectively, C_{A} and C_{B} are the concentrations in the solution (in the eluent), A is an anion in the eluent (A = $\mathrm{OH^-}$, $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$) with charge x and B is an anion in the sample with charge y. In principle, the values of $F_{\mathrm{OH^-}}$, $F_{\mathrm{HCO_3^-}}$ and $F_{\mathrm{CO_3^{2-}}}$ should not depend on the sample being analysed, *i.e.*, on the choice of B, but rather on the eluent composition used. Nevertheless, it is impossible to avoid the use of ions B in the calculations because otherwise the respective $K_{\mathrm{A}}^{\mathrm{B}}$ and D_{B} values would not be available. It is obvious that we have to calculate three kinds of quantities: $K_{\mathrm{A}}^{\mathrm{B}}$, D_{B} and C_{A}. The concentrations in the liquid phase ($C_{\mathrm{OH^-}}$, $C_{\mathrm{HCO_3^-}}$ and $C_{\mathrm{CO_3^{2-}}}$) were obtained according to ref. 4.

The partition coefficient [5]

$$D_{\mathrm{B}} = \bar{C}_{\mathrm{B}}/C_{\mathrm{B}} = (t_{\mathrm{B}} - t_0)L/v \qquad (3)$$

is related to the retention times t_{B} (for the ion under study) and t_0 (for the non-sorbed component); L is the column length and v is the linear velocity of eluent in the column. In this work, we used the retention times t_{B} for four anions ($\mathrm{Cl^-}$, $\mathrm{NO_3^-}$, $\mathrm{HPO_4^{2-}}$ and $\mathrm{SO_4^{2-}}$), each measured with 25 different carbonate eluents, employing a separation column packed with HIKS-1 ion-exchange resin [6].

Calculation of the ion-exchange constants $K_{\mathrm{A}}^{\mathrm{B}}$ is the most tedious and complicated. The method suggested in ref. 4, which applies the linear regression approach, minimizes the sum of squares along the Q/D_{B} axes. After some experimentation we found it not to be applicable to large data sets because it often yields negative equilibrium constant values. Therefore, we present an alternative method for calculating the $K_{\mathrm{A}}^{\mathrm{B}}$ values based on a non-linear regression algorithm [7]. This method minimizes the sum

$$Y = \sum (t_{\mathrm{B,calc.}} - t_{\mathrm{B,exp.}})^2 \qquad (4)$$

using some estimates for $K_{\mathrm{A}}^{\mathrm{B}}$. The latter are then varied to obtain the lowest possible value of Y [7]. It is important to point out that in the algorithm applied [7], the signs of the parameters adjusted ($K_{\mathrm{A}}^{\mathrm{B}}$) are given by the researcher. For calculation of t_{B} values using currently available $K_{\mathrm{A}}^{\mathrm{B}}$ values, we first need the partition coefficient (D_{B}) available as a root of the quadratic equation

$$aD_{\mathrm{B}}^2 + bD_{\mathrm{B}} + c = 0 \qquad (5)$$

where

$$a = 2(K_{\mathrm{CO_3^{2-}}}^{\mathrm{B}})^{-1} C_{\mathrm{CO_3^{2-}}}$$

$$b = (K_{\mathrm{OH^-}}^{\mathrm{B}})^{-1} C_{\mathrm{OH^-}} + (K_{\mathrm{HCO_3^-}}^{\mathrm{B}})^{-1} C_{\mathrm{HCO_3^-}}$$

$$c = -Q$$

Eqn. 5 was derived for the case $y = 1$ ($\mathrm{Cl^-}$ and $\mathrm{NO_3^-}$); if $y = 2$ ($\mathrm{HPO_4^{2-}}$ and $\mathrm{SO_4^{2-}}$), we have to use

$$aD_{\mathrm{B}} + bD_{\mathrm{B}}^{0,5} + c = 0 \qquad (6)$$

where

$$a = 2(K_{\mathrm{CO_3^{2-}}}^{\mathrm{B}})^{-0,5} C_{\mathrm{CO_3^{2-}}}$$

$$b = (K_{\mathrm{OH^-}}^{\mathrm{B}})^{-0,5} C_{\mathrm{OH^-}} + (K_{\mathrm{HCO_3^-}}^{\mathrm{B}})^{-0,5} C_{\mathrm{HCO_3^-}}$$

$$c = -Q$$

The D_{B} values obtained by eqn. 5 (or eqn. 6) allow us to calculate

$$t_{\mathrm{B,calc.}} = vD_{\mathrm{B}}/L + t_0 \qquad (7)$$

which is needed for Y (eqn. 4). Using the non-derivative iterative procedure [7] and the $t_{\mathrm{B,exp.}}$ values taken from ref. 6, we calculated the $K_{\mathrm{A}}^{\mathrm{B}}$ values presented in Table I. These $K_{\mathrm{A}}^{\mathrm{B}}$ values are statistically significant if A = $\mathrm{CO_3^{2-}}$ and $\mathrm{HCO_3^-}$ (except for sulphate ions if A = $\mathrm{HCO_3^-}$) and crude estimates only if A = $\mathrm{OH^-}$. This indicates that the column capacity fraction accounting for $\mathrm{OH^-}$ ions ($F_{\mathrm{OH^-}}$) is low, which results in uncertain $K_{\mathrm{OH^-}}^{\mathrm{B}}$ estimates, *i.e.*, the iterated $K_{\mathrm{OH^-}}^{\mathrm{B}}$ values depend considerably on the choice of the respective zero estimates. The constants given in Table I and partition coefficients [5] D_{B} (eqn. 3) calculated from the t_{B} values [6] were used to obtain the fractions of the capacity of the HIKS-1 resin linked to the $\mathrm{OH^-}$, $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$ ions present in the carbonate eluent used:

$$F_{\mathrm{OH^-}} = (K_{\mathrm{OH^-}}^{\mathrm{B}})^{-1} D_{\mathrm{B}} C_{\mathrm{OH^-}} Q^{-1} \qquad (8)$$

$$F_{\mathrm{HCO_3^-}} = (K_{\mathrm{HCO_3^-}}^{\mathrm{B}})^{-1} D_{\mathrm{B}} C_{\mathrm{HCO_3^-}} Q^{-1} \qquad (9)$$

$$F_{\mathrm{CO_3^{2-}}} = 2(K_{\mathrm{CO_3^{2-}}}^{\mathrm{B}})^{-1} D_{\mathrm{B}}^2 C_{\mathrm{CO_3^{2-}}} Q^{-1} \qquad (10)$$

Eqns. 8–10 are appropriate for $\mathrm{Cl^-}$ and $\mathrm{NO_3^-}$

TABLE I

ION-EXCHANGE CONSTANTS[a] CALCULATED BY THE NON-LINEAR REGRESSION METHOD

B	$K^{\mathrm{B}}_{\mathrm{OH}^-} = \dfrac{\bar{C}_{\mathrm{B}}C_{\mathrm{OH}^-}}{C_{\mathrm{B}}\bar{C}_{\mathrm{OH}^-}}$	$K^{\mathrm{B}}_{\mathrm{OH}^-} = \dfrac{\bar{C}_{\mathrm{B}}C^2_{\mathrm{OH}^-}}{C_{\mathrm{B}}\bar{C}^2_{\mathrm{OH}^-}}$	$K^{\mathrm{B}}_{\mathrm{HCO}_3^-} = \dfrac{\bar{C}_{\mathrm{B}}C_{\mathrm{HCO}_3^-}}{C_{\mathrm{B}}\bar{C}_{\mathrm{HCO}_3^-}}$	$K^{\mathrm{B}}_{\mathrm{HCO}_3^-} = \dfrac{\bar{C}_{\mathrm{B}}C^2_{\mathrm{HCO}_3^-}}{C_{\mathrm{B}}\bar{C}^2_{\mathrm{HCO}_3^-}}$	$K^{\mathrm{B}}_{\mathrm{CO}_3^{2-}} = \dfrac{\bar{C}^2_{\mathrm{B}}C_{\mathrm{CO}_3^{2-}}}{C^2_{\mathrm{B}}\bar{C}_{\mathrm{CO}_3^{2-}}}$	$K^{\mathrm{B}}_{\mathrm{CO}_3^{2-}} = \dfrac{\bar{C}^2_{\mathrm{B}}C^2_{\mathrm{CO}_3^{2-}}}{C^2_{\mathrm{B}}\bar{C}^2_{\mathrm{CO}_3^{2-}}}$
Cl^-	1.370[b]		2.23 ± 0.73		0.430 ± 0.009	
NO_3^-	0.747[b]		2.11 ± 0.12		3.890 ± 0.100	
HPO_4^{2-}		$\geqslant$10.0[b]		1.04 ± 0.06		2.15 ± 0.04
SO_4^{2-}		0.58[b]		96.0[b]		6.19 ± 0.32

[a] The presented root-mean-square errors were calculated using twelve values of $K^{\mathrm{B}}_{\mathrm{A}}$ obtained with different zero estimates.

[b] Statistically insignificant at a confidence level $P = 0.95$.

($y = 1$). For HPO_4^{2-} and SO_4^{2-} ($y = 2$), we used

$$F_{\mathrm{OH}^-} = (K^{\mathrm{B}}_{\mathrm{OH}^-})^{-0,5} D^{0,5}_{\mathrm{B}} C_{\mathrm{OH}^-} Q^{-1} \tag{11}$$

$$F_{\mathrm{HCO}_3^{2-}} = (K^{\mathrm{B}}_{\mathrm{HPO}_4^{2-}})^{-0,5} D^{0,5}_{\mathrm{B}} C_{\mathrm{HCO}_3^-} Q^{-1} \tag{12}$$

$$F_{\mathrm{CO}_3^{2-}} = 2(K^{\mathrm{B}}_{\mathrm{CO}_3^{2-}})^{-0,5} D_{\mathrm{B}} C_{\mathrm{CO}_3^{2-}} Q^{-1} \tag{13}$$

RESULTS AND DISCUSSION

The mean values of F_{OH^-}, $F_{\mathrm{HCO}_3^-}$ and $F_{\mathrm{CO}_3^{2-}}$ for all four ions considered (B) are presented in Table II. The probable errors of the calculated F_{OH^-}, $F_{\mathrm{HCO}_3^{2-}}$ and $F_{\mathrm{CO}_3^{2-}}$ values (with 24 degrees of freedom) may be calculated as follows: (i) for F_{OH^-} and $F_{\mathrm{HCO}_3^-}$, 0.5–1.0 times the value given in Table II; (ii) for $F_{\mathrm{CO}_3^{2-}}$, 0.06–0.2 times the value given in Table II. The data presented in Table II allow three conclusions to be drawn: (1) the fraction $F_{\mathrm{CO}_3^{2-}}$ is always the largest, decreasing with increasing sum of concentrations C; (2) the second large fraction is, as a rule, $F_{\mathrm{HCO}_3^-}$, increasing with increasing sum C; as expected when $C_{\mathrm{NaHCO}_3} = 0$, $F_{\mathrm{HCO}_3^-} < F_{\mathrm{OH}^-}$; (3) the fraction F_{OH^-} is the lowest, increasing with decreasing C_{NaHCO_3}; in other words, as expected, F_{OH^-} is larger for eluents with higher pH.

TABLE II

FRACTION OF THE CAPACITY OF THE HIKS-1 RESIN BONDED TO OH^- (F_{OH^-}), HCO_3^- ($F_{\mathrm{HCO}_3^-}$) AND CO_3^{2-} ($F_{\mathrm{CO}_3^{2-}}$) IONS

$\dfrac{C_{\mathrm{NaHCO}_3}}{C_{\mathrm{Na}_2\mathrm{CO}_3}}$	Fraction	$C = C_{\mathrm{NaHCO}_3} + C_{\mathrm{Na}_2\mathrm{CO}_3}$ (mM)				
		2	4	6	8	12
3.00	F_{OH^-} (%)	1.5	1.2	0.9	0.8	0.6
	$F_{\mathrm{HCO}_3^-}$ (%)	18.8	24.7	28.0	30.8	35.8
	$F_{\mathrm{CO}_3^{2-}}$ (%)	79.7	74.1	71.1	68.4	63.6
1.00	F_{OH^-} (%)	2.8	2.4	2.1	1.9	1.7
	$F_{\mathrm{HCO}_3^-}$ (%)	10.3	13.9	16.9	19.0	23.5
	$F_{\mathrm{CO}_3^{2-}}$ (%)	86.9	83.7	81.0	79.1	74.8
0.50	F_{OH^-} (%)	4.4	3.7	3.3	3.1	3.0
	$F_{\mathrm{HCO}_3^-}$ (%)	7.8	9.6	11.1	12.5	16.1
	$F_{\mathrm{CO}_3^{2-}}$ (%)	87.8	86.6	85.6	84.5	80.9
0.33	F_{OH^-} (%)	5.2	4.6	4.2	3.9	3.9
	$F_{\mathrm{HCO}_3^-}$ (%)	6.6	7.9	8.8	9.9	12.6
	$F_{\mathrm{CO}_3^{2-}}$ (%)	88.2	87.5	87.0	86.2	83.5
0.00	F_{OH^-} (%)	7.8	8.0	7.8	8.3	9.7
	$F_{\mathrm{HCO}_3^-}$ (%)	3.9	4.1	4.1	4.2	4.9
	$F_{\mathrm{CO}_3^{2-}}$ (%)	88.3	87.9	88.1	87.5	85.4

These conclusions apply to the HIKS-1 resin, for which ion-exchange occurs on $-\mathrm{CH}_2\mathrm{N}^+(\mathrm{CH}_3)_3$ groups. It is to be expected that the behaviour of F_{OH^-}, $F_{\mathrm{HCO}_3^-}$ and $F_{\mathrm{CO}_3^{2-}}$ for other resins with the same functional group will be similar to that for HIKS-1.

The computer programs used were written in Fortran-4 and are available on request.

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