

Retention mechanism of anions in micellar chromatography: Interpretation of retention data on the basis of an ion-exchange model

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Abstract

Micellar chromatography is an effective method not only for organic separations but also for inorganic separations because of its unique selectivity. Although a pseudo-phase model is widely utilized in the interpretation of the retention of neutral organic compounds, there is some ambiguity in applying this model to the quantitative description of the micellar chromatographic behaviour of inorganic ions. In this paper, a novel retention model based on a stoichiometric ion-exchange model is developed to elucidate the retention behaviour of anions in cationic micellar chromatography. The developed model involves the dissociation constant of a counter ion from a micelle and two ion-exchange equilibrium constants at the interfaces between the solution and micelles and between the solution and stationary phase.

1. Introduction

Secondary equilibria have promised effectiveness in varying and enhancing liquid chromatographic selectivity [1]. Partition to a micellar phase, which has been successfully utilized in organic liquid chromatography [1,2], is one of the representatives of secondary equilibria. It is well known that, in micellar chromatographic separations of organic compounds, a pseudo-phase retention model describes the experimental results well, where the hydrophobic or lipophilic partitioning of electroneutral analytes into a micellar pseudo-phase is thought to be an important factor in determining retention [2,3]. If both an analyte and a micelle are ionic, electrostatic interactions rather than hydro-

phobic partitioning will be dominant in the retention mechanisms.

Although the use of micellar mobile phases has rarely been applied in inorganic chromatography, it is known that even in this application micellar mobile phases enhance the selectivity of separation [4–7]. Fig. 1 shows chromatograms of some inorganic anions. The elution order of ions can be altered not only by varying the micellar concentration but also by changing the concentration of added salts.

The aim of this paper is to explain quantitatively the behaviour of inorganic anions in cationic micellar chromatography. The partition of ions to oppositely charged micelles can be represented by an ion-exchange model, although micelles are not static but dynamic [8,9]. Various ion-exchange models have been reported [10–15], of which a stoichiometric ion-exchange model [13] is the most common. Although it has

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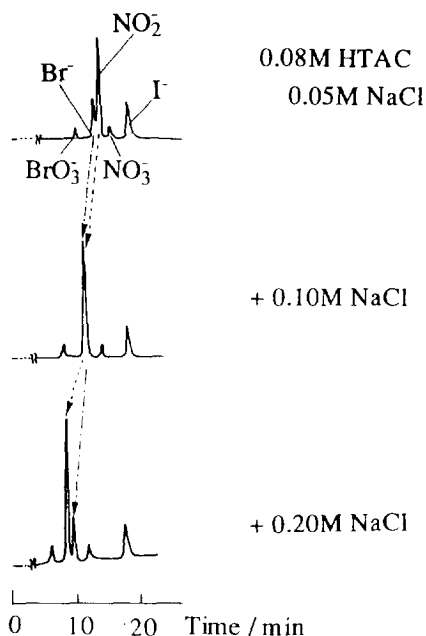


Fig. 1. Micellar chromatograms of some inorganic anions. Detection at 215 nm. Mobile phases are given on the right of each chromatogram.

recently been indicated that a stoichiometric ion-exchange model does not describe ion-exchange processes in a strict sense [10–12], this model has been extensively used and successfully explains not only the retention mechanisms of ions in ion-exchange chromatography [13] but also the behaviour of counterions of micelles [8,9]. In a previous paper [6], we succeeded in developing a model capable of describing the retention behaviour of cations in sodium dodecylsulfate (SDS) micellar chromatography. As the separation of transition metal ions by SDS micellar chromatography required the addition of a suitable ligand to the mobile phase, the mobile phase necessarily contained salts at concentrations high enough to neglect the dissociation of counter ions from SDS micelles. In this paper, we attempt to interpret the retention behaviour of anions in cationic micellar chromatography using a stoichiometric ion-exchange model. Not only does this model elucidate the applicability of a stoichiometric ion-exchange model but also it allows the evaluation of the dissociation of counter ions from micelles.

2. Experimental

The chromatographic system was composed of a Tosoh computer-controlled CCPD pump, a Rheodyne injection valve equipped with a 100- μ l sample loop, a JASCO Model 875-UV, UV-visible detector and a recorder. A Wakosil 5C8 stainless-steel column (150 mm \times 4.6 mm I.D.) packed with 5- μ m octylsilylated silica gel, with specific surface area 300 m² g⁻¹, carbon content 12% and carbon coverage 1.29 μ mol m⁻², was used. Data were processed on a NEC PC-9801 personal computer.

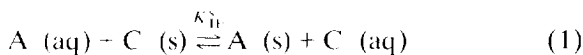
Hexadecyltrimethylammonium chloride (HTAC) was recrystallized from acetone-methanol and dried over P₂O₅ under vacuum after rinsing with diethyl ether. Distilled, deionized water was used. Other reagents were of analytical-reagent grade.

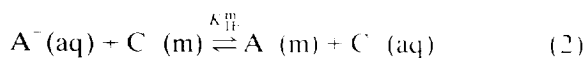
The amounts of HTAC adsorbed on the column were determined by ion-pair extraction as follows: the column was equilibrated with a solution containing HTAC and in some instances NaCl; after adsorption equilibrium had been established, the column was rinsed well with methanol; after evaporation of the methanol, acetate buffer and Orange II solution were added to the residue; the ion pair of HTAC and Orange II was extracted into chloroform and the absorbance of the chloroform phase was measured spectrometrically. After correcting for the moles of HTAC existing in the dead volume of the column, the amount of adsorbed HTAC was calculated. Column dead volumes were determined by a method described by Shibukawa and Ohta [16].

3. Results and discussion

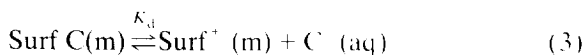
3.1. Retention model

Assuming monovalent anions as analytes for simplicity, we took the following ion-exchange equilibria into account to derive the equation describing of the retention of anions:





where A^- and C^- are an analyte and a counter anion, respectively, s, aq and m in parentheses denote stationary, solution and micellar phase, respectively, and K_{IE}^s and K_{IE}^m are the ion-exchange equilibrium constants at the solution–resin and solution–micelle interface, respectively. Counter ions are not fully bound to micelles, but are partly dissociated: this causes mass action in ion-exchange equilibria even in the absence of added salts. The dissociation of counter ions is given by



$$K_d = [\text{Surf }^+(m)][C^-(aq)]/[\text{Surf } C(m)]$$

where $\text{Surf } C(m)$ and $\text{Surf }^+(m)$ denote a surfactant forming an ion pair with a counter ion and that existing as a cation in the micelles, respectively.

The capacity factor of an analyte is represented by

$$k' = \phi[A^-(s)]/([A^-(aq)] + [A^-(m)]\bar{v}C_M) \quad (4)$$

where ϕ is the phase ratio, \bar{v} is the molal volume of micelles and C_M is the micellar concentration; these are introduced to convert the micellar phase concentration of an analyte into the solution phase concentration. Substitution of equilibrium constants in Eq. 4 gives

$$\frac{\phi}{k'} = \frac{[C^-(aq)]}{K_{IE}^s[C^-(s)]} \left\{ 1 + \frac{K_{IE}^m C_M}{[C^-(aq)] + K_d} \right\} \quad (5)$$

Free counter ions in solution come from (1) the dissociation of micelles (C_{dis}^-), (2) the counter ions of monomeric surfactants [equal to the critical micellar concentration (cmc) of a micelle] (C_{cmc}^-), and (3) added salts (C_{add}^-):

$$[C^-(aq)] = [C_{dis}^-] + [C_{cmc}^-] + [C_{add}^-] \quad (6)$$

The second and third terms in Eq. 6 are known, and $[C_{dis}^-]$ can be calculated if K_d is known. Eq. 5 can therefore represent the retention of anions in any case.

3.2. Calculation of equilibrium constants involved in the above retention model

The validity of the above model was verified both in the presence and in the absence of an added salt. A single anion system was assumed for simplicity; NaCl was used as an added salt. In the presence of a large amount of added salts, $[C^-(aq)]$ can be regarded as equal to $[C_{add}^-]$, because $[C_{cmc}^-]$ is not more than 1.3 mM (equal to cmc of HTAC; usually the cmc is lowered by the addition of salts), and $[C_{dis}^-]$ is also neglected as K_d is very small, as shown below. If $K_d \ll [C^-(aq)]$, plots of $\phi/k'[C^-(aq)]$ vs. $1/[C^-(aq)]$ will be linear at any constant C_M . Fig. 2 shows example plots obtained at $C_M = 0.08 M$. In order to facilitate the determination of K_{IE}^s , Eq. 5 was changed into the following form in the plots depicted in Fig. 2:

$$\frac{n_{Cl(s)}}{(V_r - V_0)[Cl^-(aq)]} = \frac{1}{K_{IE}^s} \left\{ 1 + \frac{K_{IE}^m C_M}{[Cl^-(aq)]} \right\} \quad (5')$$

where $n_{Cl(s)}$ is the moles of a counter ion in the stationary phase, which is equal to the moles of adsorbed HTAC on the stationary phase, and V_r

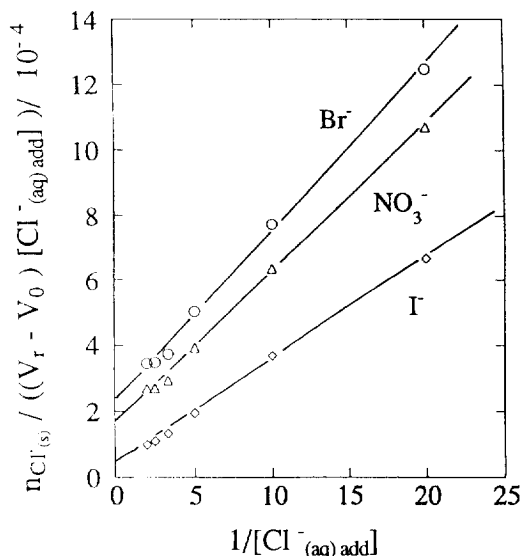


Fig. 2. Examples of linear plots based on Eq. 5. Details are given in the text.

and V_0 denote the retention volume of an analyte and the void volume of the column, respectively. The constancy of $n_{C(s)}$ was confirmed by the determination of the amount of HTAC adsorbed on the column as follows: 0.66 mmol with 0.1 M NaCl, 0.67 mmol with 0.2 M NaCl, 0.68 mmol with 0.3 M NaCl and 0.66 mmol with 0.5 M NaCl. Table 1 lists ion-exchange constants obtained at $C_M = 0.06$ and 0.08 M. Similar values were obtained for both micellar concentrations, indicating the validity of the model developed.

On the other hand, in the absence of an added salt, $[C^-(aq)] = [C_{dis}^-] + [C_{cmc}^-]$. As CMC is constant (1.3 mM) regardless of C_M , $[C^-(aq)]$ is a function of C_M alone. We can therefore determine K_d and the ion-exchange equilibrium constants by applying non-linear regression based on the reciprocal form of Eq. 5 to experimental data set of k' and C_M . Fig. 3 shows example plots of $V_r - V_0$ vs C_M , and Table 2 lists equilibrium constants obtained with non-linear regression.

K_d is almost constant, and the ion-exchange equilibrium constants agree well with values listed in Table 1.

3.3. Relationship between the retention model developed and a pseudo-phase model

The equilibrium constants listed in Tables 1 and 2 permit the calculation of partition coefficients, which are used in a pseudo-phase retention model:

Table 1
Ion-exchange equilibrium constants obtained on the basis of Eq. 5

Ion	$C_M = 0.06 M$		$C_M = 0.08 M$	
	K_{IE}^m	K_{IE}^s	K_{IE}^m	K_{IE}^s
BrO_3^-	1.44	1.79	1.37	1.77
Br	3.09	4.63	2.77	4.32
I^-	13.2	33.2	12.1	30.1
NO_2^-	1.71	2.05	1.74	2.16
NO_3^-	3.55	6.21	3.53	6.17

$[Cl_{add}]$ was changed from 0.05 to 0.5 M.

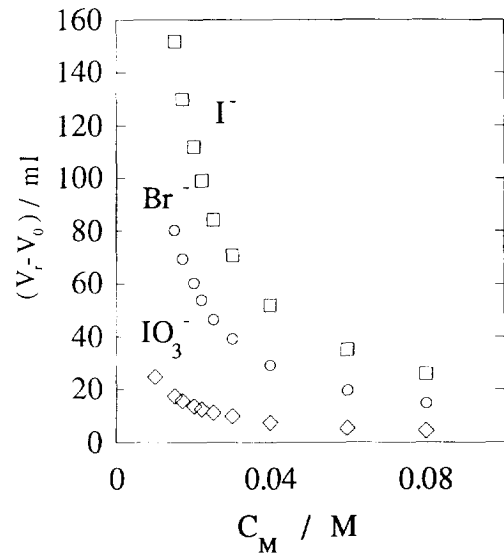


Fig. 3. Relationships between $(V_r - V_0)$ and C_M . Non-linear regression was applied to these relationships to determine K_{IE}^m , K_{IE}^s , and K_d . Details are given in the text.

$$K_{SW} = [A^-(s)]/[A^-(aq)] = K_{IE}^s [C^-(s)]/[C^-(aq)] \quad (7)$$

$$K_{MW} = [A^-(m)]/[A^-(aq)] = K_{IE}^m [C^-(m)]/[C^-(aq)] = K_{IE}^m / \bar{v} ([C^-(aq)] + K_d) \quad (8)$$

where K_{SW} and K_{MW} are partition coefficients of an analyte between the solution and stationary phase and between the solution and micellar phase, respectively. According to our model, both partition coefficients are not constant but

Table 2
Ion-exchange equilibrium constants and the dissociation constant of Cl⁻ from HTAC micelles

Ion	K_{IE}^m	K_{IE}^s	K_d
BrO_3^-	1.4	2.0	$6.9 \cdot 10^{-4}$
Br	2.8	4.8	$6.5 \cdot 10^{-4}$
I	13	36	$6.1 \cdot 10^{-4}$
NO_2^-	1.7	2.2	$6.7 \cdot 10^{-4}$
NO_3^-	3.4	6.4	$6.8 \cdot 10^{-4}$

functions of $[C^-(aq)]$. If a large amount of salts is added, $[C^-(aq)]$ becomes constant and hence the partition coefficients also become constant. This situation is clearly shown in Figs. 4 and 5. Fig. 4 shows the changes in K_{MW} , K_{SW} and $(K_{MW} - 1)/K_{SW}$ with C_M in the absence of added salts. $(K_{MW} - 1)/K_{SW}$ is the slope of a plot based on a pseudo-phase model represented by [2]

$$1/(V_r - V_0) = (K_{MW} - 1)\bar{v}C_M/V_s K_{SW} \quad (9)$$

where V_s is the volume of the stationary phase. Both partition coefficients increase with decrease-

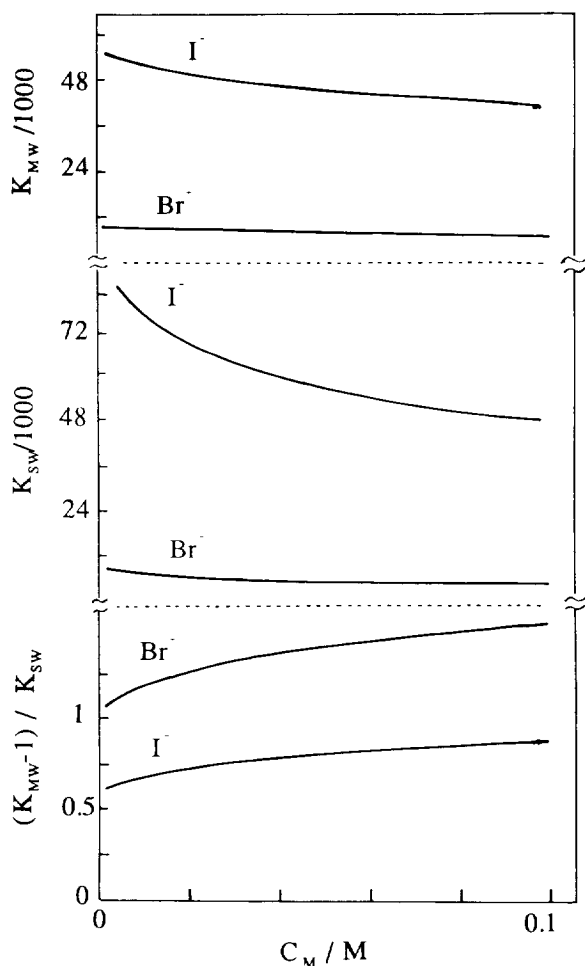


Fig. 4. Changes in K_{MW} , K_{SW} and $(K_{MW} - 1)/K_{SW}$ with C_M in the absence of an added salts. These values were calculated according to Eqs. 7 and 8.

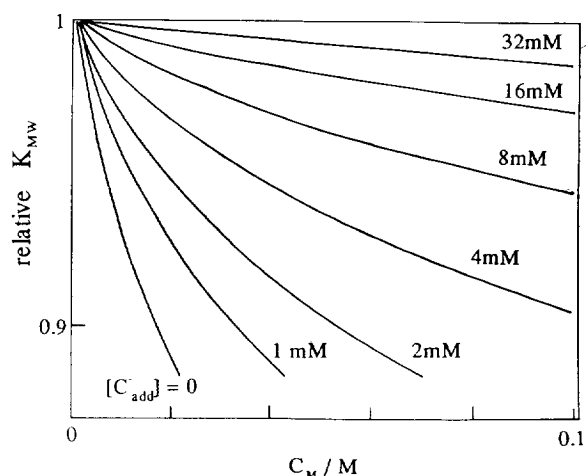


Fig. 5. Changes in K_{MW} for I^- with $[C_{add}^-]$. Relative K_{MW} with respect to that at $C_M \rightarrow 0$ is plotted against C_M . Eq. 7 was used for calculation.

ing C_M , because $[C^-(aq)]$ decreases with decreasing C_M . $(K_{MW} - 1)/K_{SW}$, in contrast, decreases with decreasing C_M ; the change in this value is much smaller than those in the partition coefficients. This indicates that a plot based on Eq. 9 seems linear at high micellar concentrations, but that it is actually concave rather than linear.

Fig. 5 shows the effect of added salts on the partition coefficients, where K_{MW} for I^- is taken as an example and relative K_{MW} is plotted against C_M . It is obvious that K_{MW} becomes constant as the salt concentration increases.

In conclusion, the developed model implies that the retention of ions in ionic micellar chromatography can be described by a stoichiometric ion-exchange model, and formally obeys a pseudo-phase model when the concentration of an added counter-ion is high enough to neglect the concentration of the counter-ion coming from the dissociation of micelles.

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