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Charged surface and mass transfer in dynamic ion exchangers

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ABSTRACT

Ion-interaction reagents (IIR) were used in both static (presorbed as fixed-site charges) and dynamic modes on C_{18} silica bonded phases to evaluate the sorption mechanisms for inorganic ions in "ion pairing systems". Column break-through techniques were used to determine the shifts in the sorption equilibria of the IIR as a result of the sorption of the analyte. The results showed that the changes in the sorption isotherm of the IIR were linearly related to the amount of analyte retained on the stationary phase, even for loadings up to 25% of the total capacity (0.26 mequiv. of IIR per ml of column volume); this behaviour is consistent with theoretical models previously reported for a dynamic ion-exchange mechanism. Studies of the ion-exchange constant, K_{IEX}, for the sorption of inorganic ions onto the charged surface of the reversed-phase, have shown that the magnitude of K_{IEX} depends on the amount of IIR sorbed. The relationship was essentially the same for both static and dynamic separation modes, and was similar to patterns reported for K_{IEX} for inorganic ions as a function of ion-exchange capacity in conventional resins.

INTRODUCTION

Dynamic ion-exchange or ion-pairing techniques have been used extensively for the separation of organic and inorganic analytes. Studies on the mechanism of sorption of organic analytes in these systems has been the subject of several papers. Experimental results reported by Schill and co-workers [1–3] have shown that the equilibration of an organic analyte and an ion interaction reagent (IIR) with the stationary phase (SP) are related to each other in a complex fashion. The most important features of these expermental studies are that the introduction of the analyte ion (A^{n+}) causes changes in the concentration of the IIR relative to the mobile phase (MP) concentration; and that the magnitude and sign of these changes is dependent upon A^{n+} and system peak (IIR) retention. Other experimental studies on these systems have reported unusual peak behaviour such as peak splitting and deformations, and these effects have been explained with a model based on multiple retention mechanisms or a gradient in the IIR during the elution of the analyte peak [4–6].

Several mathematical treatments that predict some of the features of dynamic ion-exchange systems have been reported [7–13], but these treatments have not provided a complete chemical interpretation of the mechanism of the sorption process. Theoretical studies by Stranahan and Deming [9] have provided an explanation of the direction of the peak response for the IIR observed by indirect detection, but did not

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explain the changes in the signal intensity with retention of A^{n+} and system peak. Other theoretical studies have developed mathematical expressions relating the signal intensity to the retention of A^{n+} and the system peak [10–13], but these treatments have not provided a clear chemically based description as to why these changes occur.

Recently, we have made use of selective detection of the IIR (indirect detection method) and A^{n+} (inorganic ions) to provide a better understanding of the equilibria occurring in these systems [14]. With the results of these experimental measurements and simulations based on a simple Craig distribution model it was possible to provide a chemically based explanation for the peak response patterns and signal intensity changes in the IIR as a function of retention of the IIR and A^{n+}. The model was also used to explain how separation problems such as peak splitting could be eliminated. These studies also examined the relationship of the amount of excess IIR adsorbed, which is caused by injection of A^{n+}, with the amount of A^{n+} injected. However, the results were not accurate enough to clearly define how the ratio, moles excess IIR_{SP} to moles A^{n+} injected, changed with retention of A^{n+} and IIR (system peak). Consequently one aim of our present studies was to determine, using column breakthrough techniques with selective detection for the analyte and IIR, how the adsorption of excess IIR changed with amount of A_{SP}^{n+} and retention of A^{n+}.

Recent studies by Liu and Cantwell [15] on a model based on an electrical double layer for dynamic ion exchange have shown that for small organic analytes the dominant mechanism of sorption is ion exchange rather than adsorption. For the small organic solutes studied by Liu and Cantwell the coefficient for ion exchange, K_{IEX}, was determined to be a constant with amount of IIR adsorbed. However, Fritz and Story [16] have shown that K_{IEX} for inorganic ions on conventional ion-exchange resins changes with the ion-exchange capacity. Consequently, we wanted to determine K_{IEX} by direct detection methods to see if similar changes in the ion-exchange constant could occur in dynamic and fixed-site ion-exchange systems, and if these changes in K_{IEX} might alter the sorption process.

EXPERIMENTAL

Equipment and chemicals

The detector was a Waters 990 photodiode array detector (Waters Division of Millipore, Missauga, Canada). The pumps were Waters 510 pumps and the injector was a Rheodyne 7125 (Rheodyne, Cotati, CA, U.S.A.). The column was a Supelcosil 5-μm LC-18 column (150 × 4.6 mm I.D., C_{18} bonded to silica, Supelco, Oakville, Canada) or Waters 5-μm Radial-Pak C_{18} column (100 × 8.0 mm I.D., C_{18} bonded to silica). The IIR was 4-octylbenzenesulfonic acid (4-OBS) (Aldrich, Milwaukee, WI, U.S.A.). Complexing agents, which were added to the mobile phase, were tartaric acid (Aldrich) and α-hydroxyisobutyric acid (Sigma, St. Louis, MO, U.S.A.). The postcolumn reagent used for detection of metal ions was 4-(2-pyridylazo)resorcinol monosodium salt ($2.0 \cdot 10^{-4}$ mol l^{-1} PAR, 1.0 mol l^{-1} ammonium acetate, 2.0 mol l^{-1} ammonium hydroxide, Aldrich).

PROCEDURE AND CALCULATIONS

Mole ratio IIR to A^{n+} studies

A mobile phase containing 1.71 m*M* 4-octylbenzenesulfonic acid, 0.10 *M* α-hydroxyisobutyric acid (pK_a = 4.03 [17]), at pH 3.90 and sodium chloride was passed through a Supelcosil 5-μm C_{18} column at 1.0 ml min^{-1}. The ionic strength of the mobile phase was selected to be $1.225 \cdot 10^{-1}$ *M*. Sodium chloride was used to compensate for varying amounts of metal ion present in the mobile phase. Equilibration of the column with mobile phase was verified by the breakthrough curve for the IIR reagent by monitoring the absorbance of the IIR (4-octylbenzenesulfonic acid) at 260 nm with a photodiode array detector. Once equilibration was reached the mobile phase was changed to one containing metal ion (at constant ionic strength) and the breakthrough curve for the IIR was determined. The breakthrough curve for A^{n+} was determined by monitoring the absorbance of the metal–PAR complex after postcolumn reaction with PAR (at 520 nm). Helium gas was used to introduce the postcolumn reagent into the eluent at a flow-rate of 0.5 ml min^{-1} via a low-dead-volume mixer. The analyte ions (Cd, Mg and Mn) were selected as analytes on basis of their retention characteristics and solubility properties in surfactant solutions.

Fixed-site ion exchangers

Fixed-site ion exchangers were prepared by coating a 5-μm C_{18} Supelcosil (at 1.0 ml min^{-1}) or a Waters Radial-Pak column (at 2.0 ml min^{-1}) with an arachidyl sulfate (C_{20} sulfate) acetonitrile solution, followed by equilibration with a mobile phase containing a complexing agent (≈ 150 ml). The column was stripped with acetonitrile–deionized water (50:50, v/v) solution and measurements of the dry mass of arachidyl sulfate adsorbed onto the stationary phase were made by constant weight analysis.

Preparation of dynamic ion exchangers

The dynamic ion exchangers were prepared by equilibration of a mobile phase containing 4-octylbenzenesulfonic acid and a complexing agent (α-hydroxyisobutyric acid). The concentration of α-hydroxyisobutyric acid, pH, and column (LC-18 5-μm C_{18} column, Supelcosil) were selected to be the same as one of the fixed-site systems for purposes of comparison of different types of ion exchangers. The mass of 4-octylbenzenesulfonic acid loaded onto the stationary phase was determined from the breakthrough curve of 4-octylbenzenesulfonic acid.

CALCULATIONS

Relative ion-exchange constant ($K_{\mathrm{IEK,R}}$)

A relative ion-exchange constant, $K_{\mathrm{IEX,R}}$, which can be used to evaluate relative changes in selectivity with ion-exchange capacity for a given set of eluent conditions, was calculated as follows:

$$K_{\mathrm{IEX,R}} = \frac{K_{\mathrm{IEX}}}{[\mathrm{E}^+]^n_{\mathrm{MP}}} = \frac{[\mathrm{A}^{n+}]_{\mathrm{SP}}}{[\mathrm{E}^+]^n_{\mathrm{SP}}\,[\mathrm{A}^{n+}]_{\mathrm{MP}}} = \frac{k'_{\mathrm{A}}}{(m_{\mathrm{IX}})^n} \qquad (1)$$

where K_{IEX} is the ion-exchange selectivity constant; MP and SP are mobile and stationary phase respectively; A^{n+} is the uncomplexed analyte ion; n is the charge of the analyte ion; k'_{A} is the capacity factor of the analyte ion; E^+ is the counterion of the ion exchanger; $[E^+]_{\mathrm{MP}}$ was held constant under the experimental conditions selected by maintaining constant pH and complexing agent concentration; and m_{IX} is the concentration (g per column volume) of the ion-exchange reagent (arachidyl sulfate or 4-octylbenzenesulfonate) adsorbed onto the stationary phase. The loading of metal ion was small and thus

$$\begin{aligned}[E^+]_{\mathrm{SP}} &= \text{total capacity} - [A^{n+}]_{\mathrm{SP}} \\ &\approx \text{total capacity} = m_{\mathrm{IX}}\end{aligned} \tag{2}$$

Since the concentration of the complexing reagent in the eluent was held constant, the relative distribution of the different metal species was also constant, and thus, the effect of this is also included in $K_{\mathrm{IEX,R}}$. The capacity factors (k'_{A}) were determined by injection of 100 ng of metal ion onto a column containing known amounts of arachidyl sulfate or 4-octylbenzene sulfonate sorbed on the packing.

RESULTS AND DISCUSSION

Mole ratio IIR to A^{n+}

The breakthrough curve for the metal ion and IIR (4-OBS) in the presence of a metal ion is shown in Fig. 1. The absorbance of the metal–PAR complex remains at baseline until equilibration of the metal ion between the mobile and stationary phase is reached. At equilibrium of the metal ion, the absorbance from the metal–PAR complex increases to a maximum (≈ 40 min) and then remains constant, as shown in Fig. 1. The absorbance of the IIR decreases (≈ 40 min) when equilibration of the metal

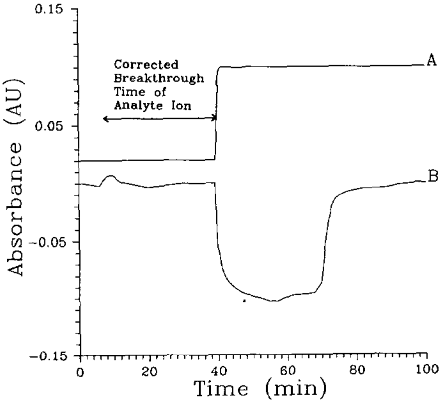

Fig. 1. Breakthrough curves for analyte ion and 4-octylbenzene sulfonic acid. Experimental conditions: 150 × 4.6 mm I.D. Supelcosil 5-μm C_{18} column; flow-rate mobile phase is 1.0 ml min^{-1}; flow-rate PAR for curve A is 0.5 ml min^{-1}; time = 0 eluent, 1.71 m*M* 4-octylbenzenesulfonic acid–0.1 *M* α-hydroxyisobutyric acid–78.59 m*M* sodium chloride, pH 3.90 with NH_4OH; time = 5.0 min eluent, 1.71 m*M* 4-octylbenzene sulfonic acid–0.1 *M* α-hydroxyisobutyric acid–1.09 m*M* manganese–74.33 m*M* sodium chloride, pH 3.90 with NH_4OH. Curve A analyte ion; curve B 4-octylbenzenesulfonic acid; *Y*-scale for curve A reduced by factor of 5.

ion is reached. This corrected breakthrough time, as labelled in Fig. 1, can be used to determine the moles of analyte ion adsorbed onto the stationary phase per column volume as follows:

$$A_{SP}^{n+} = \text{corrected breakthrough time} \cdot \text{flow-rate} \cdot [\text{analyte ion}]$$

The decrease in absorbance of the IIR (40–80 min) is caused by adsorption of excess IIR when A^{n+} is sorbed onto the stationary phase. The absorbance returns to the baseline when an equilibrium of the IIR is reached between mobile and stationary phases. Under normal elution conditions when $k'A^{n+} < k'$system peak a negative response or a decrease in the concentration of the IIR is observed [4–6], but these results show that excess IIR is adsorbed onto the stationary phase in the presence of analyte, even when $k'A^{n+} < k'$system peak. The amount of excess IIR_{SP} per column volume was determined from the absolute area of the rectangular breakthrough curve by converting the absorbance scale to concentration with Beer's law. The data obtained from these measurements are given in Fig. 2 for analyte ion concentrations ranging from 0.66 m*M* to 15.3 m*M*.

Fig. 2 (curves E, F, G and H) show that IIR_{SP} increases with A_{MP}^{n+} and with the capacity factor of A^{n+} (k'Cd < k'Mg < k'Mn for $k'A^{n+} < k'$sytem peak at mobile phase pH 3.90, and k'Mn > k'system peak at pH 3.15). These results show that the introduction of A^{n+} into the mobile phase causes an enhanced adsorption of IIR on the stationary phase as a result of partial neutralization of the charge at the eluent–sorbent interface by A^{n+}. As the retention of A^{n+} increases A_{SP}^{n+} increases, and, consequently, the amount of excess IIR_{SP}. Fig. 2 also shows that these curves become non-linear at higher analyte ion loadings, which is the result of overload conditions.

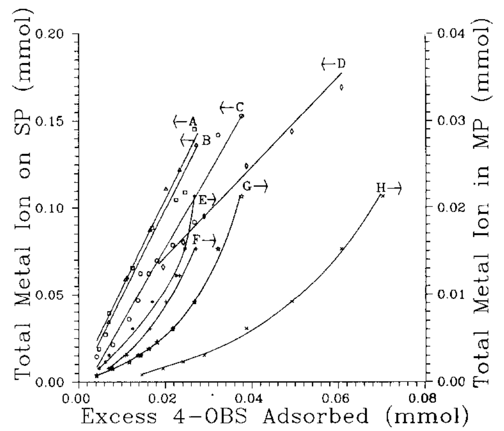

Fig. 2. The variation of moles metal ion with excess moles 4-octylbenzene sulfonic acid adsorbed on sorbent. Curves A, B, C and D *Y*-scale is total metal ion present on column; curves E, F, G and H *Y*-scale total metal ion present in the mobile phase. Curve A, E k'Cd = 13.7; curve B, F k'Mg = 23.1; Curve C, G k'Mn = 26.0; k'system peak = 37.3; Curve D, H k'Mn = 61.0 and k'system peak = 37.7. Experimental conditions: 150 × 4.6 mm I.D. Supelcosil 5-μm C_{18} column; flow-rate 1.0 ml min^{-1}; eluent, 1.71 m*M* 4-octylbenzenesulfonic acid–0.1 *M* α-hydroxyisobutyric acid, (78.59 − 4*x*) m*M* sodium chloride–*x* m*M* analyte ion, pH adjusted with NH_4OH to 3.90 for $k'_A < k'$system peak and 3.15 for $k'_A > k'$system peak.

TABLE I

AVERAGE MOLE RATIO EXCESS IIR_{SP} TO A_{SP}^{n+}

A^{n+} [a]	$k'A^{n+}$ [b]	k'sys[b]	Ionic strength (mM)	Mole ratio excess IIR_{SP}/A_{SP}^{n+} ($\pm$ S.D.)	No. of data points
Manganese	26.0	37.3	122.5	0.23 ± 0.01	11
Cadmium	13.7	37.3	122.5	0.21 ± 0.03	8
Magnesium	23.1	37.3	122.5	0.19 ± 0.01	7
Manganese	61.0	37.7	91.8	0.34 ± 0.05	7

[a] Analytes were added to the mobile phase in the concentration range of 0.66 to 15.3 mM.

[b] Analyte retention times under elution conditions with a mobile phase containing no metal ion.

However, Fig. 2 (curves A, B, C and D) shows that, even for loadings up to 25% of the total capacity (0.26 mequiv. of IIR per ml of column volume), there is a linear relationship between the excess IIR_{SP} and A_{SP}^{n+}. Thus the mole ratio of excess 4-octylbenzene sulfonate sorbed to A_{SP}^{n+} is independent of the amount of analyte sorbed on the stationary phase. Table I shows the average mole ratio of excess IIR_{SP} to A_{SP}^{n+}. This table shows that for conditions of constant ionic strength that the mole ratio is to a first approximation independent of retention of A^{n+}. This is due to the fact that the sorption of A^{n+} onto the stationary phase causes a fixed amount of IIR to be adsorbed onto the stationary phase in order compensate for the partial neutralization of the charge at the eluent–sorbent interface, which is caused by sorption of A^{n+} onto the stationary phase.

Changes in the mole ratio of IIR_{SP} to A_{SP}^{n+} can be observed when the ionic strength of the mobile phase is changed. Table I shows that the mole ratio for manganese increases when the retention time for manganese is adjusted to elute after the system peak. The changes in the mole ratio are due to a decrease in ionic strength of the mobile phase from $1.225 \cdot 10^{-1}$ M to $9.180 \cdot 10^{-2}$ M when the pH of the mobile phase was adjusted from 3.90 to 3.15 to increase the retention time of manganese. When the ionic strength is decreased the metal ion is more effective at neutralizing the charge at the eluent–sorbent interface, and thus a large amount of excess IIR is adsorbed onto the sorbent, which causes the mole ratio of excess IIR to A_{SP}^{n+} to increase.

Equilibrium constants for ion exchange in fixed-site and dynamic ion-exchange systems

The retention of small organic ions in dynamic ion-exchange systems has been described by Liu and Cantwell [15] based on a model of an electrical double-layer that exists between the mobile phase and the stationary phase. His model showed that the retention of these analytes was controlled primarily by ion-exchange rather than by adsorption processes. In his model it was determined that the coefficient for ion exchange, K_{IEX}, for small organic solutes studies was approximately constant with the loading of IIR on the sorbent.

Figs. 3 and 4 show the variation in $K_{IEX,R}$ (see Calculations) with loading of surfactant for fixed-site ion exchange on two reversed-phase systems. The magnitude of $K_{IEX,R}$ decreases to a minimum at capacities of 0.1 to 0.3 μmol g^{-1} and then begins to

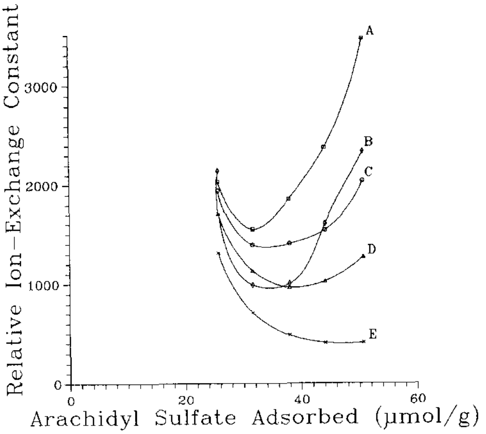

Fig. 3. Change in the relative ion-exchange constant with ion-exchange capacity (loading of ion-interaction reagent) for a fixed-site ion exchanger. Experimental conditions: 100 × 8 mm I.D. 5-μm C_{18} Waters Radial-Pak column; flow-rate 2.0 ml min^{-1}; eluent, 0.05 *M* tartaric acid, pH 3.40; sample size approximately 100 ng metal ion, Curves: A = manganese, B = lanthanum, C = nickel, D = lead, E = ytterbium. *Y*-scale for La and Yt reduced by factor of 40 and for manganese by factor of 1.5.

increases at higher capacities. The general shape of these curves are in agreement with the results reported by Fritz and Story [16] for sulfonated highly cross-linked macroporous polystyrene resins with capacities 0.23 to 3.70 μmol g^{-1}. The differences between the two curves in Figs. 3 and 4 are due to variation in pH, and complexing agent (tartaric acid and α-hydroxyisobutyric acid present in the mobile phase) and the resulting changes in $[E^+]_{MP}$ and consequently the value of $K_{IEX,R}$. The different reversed-phase columns may by also cause changes in the magnitude of $K_{IEX,R}$.

Fig. 5 shows that in dynamic ion-exchange systems the relative ion-exchange

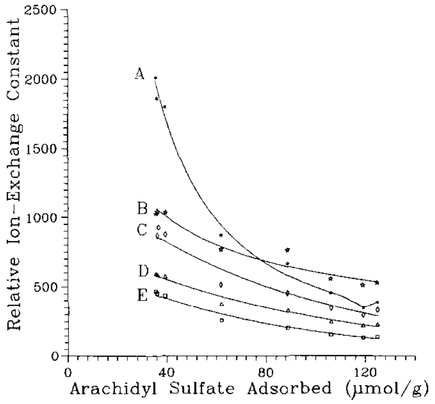

Fig. 4. Change in the relative ion-exchange constant with ion-exchange capacity for a fixed-site ion exchanger. Experimental conditions: 150 × 4.6 mm I.D. 5-μm C_{18} Supelcosil column; flow-rate 1.0 ml min^{-1}; eluent, 0.20 *M* α-hydroxyisobutyric acid pH 3.92; sample size approximately 100 ng metal ion, Curves: A = lanthanum, B = manganese, C = lead, D = cobalt, E = nickel. *Y*-scale La reduced by factor of 20.

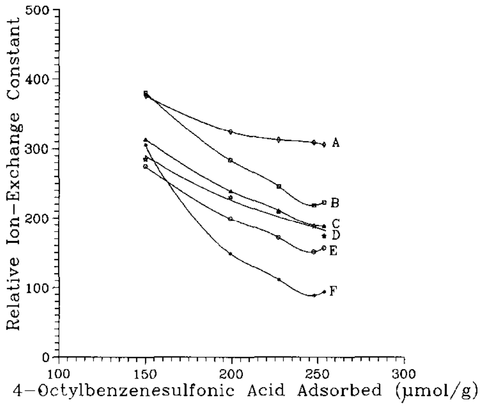

Fig. 5. Change in the relative ion-exchange constant with ion-exchange capacity for dynamic ion exchanger. Experimental conditions: 150 × 4.6 mm I.D. 5-μm C_{18} Supelcosil column; flow-rate 1.0 ml min^{-1}; eluent, x mM 4-octylbenzenesulfonic acid–0.20 M α-hydroxyisobutyric acid, pH 3.90; sample size approximately 100 ng metal ion, Curves: A = lead (scale factor 0.5), B = nickel, C = cobalt (scale factor 0.5), D = manganese (scale factor 0.2), E = zinc, F = copper (scale factor 4).

constant is also not constant with loading of surfactant. Comparison of Figs. 4 and 5 show that the relationship of $K_{IEX,R}$ to IIR loading is similar for both fixed-site and dynamic ion exchangers.

Determination of retention mechanism for inorgaic analytes

In Liu and Cantwell's [15] electrical double layer model the ion-exchange distribution coefficient, $K_{S,IEX}$, is calculated as follows:

$$K_{S,IEX} = K_{IEX} A_{SP} \Gamma_{TBA^+}/c \quad (3)$$

where K_{IEX} for the small organic anion p-nitrobenzenesulfonate (NBS^-) was determined to be a constant; A_{SP} is the area of the stationary phase; Γ_{TBA^+} is the surface excess of tetrabutylammonium ion; and c is the ionic strength. However, from the results reported here, K_{IEX} for inorganic solutes does not remain constant. Consequently the potential effect of a variation inK_{IEX} on the distribution coefficient for ion exchange was determined using the maximum variation in K_{IEX} found with the dynamic ion-exchange system. The maximum variation in $K_{IEX,R}$ was that found for Cu which is given by $K_{IEX,R} = -0.0152x + 3.8691$ where x is the amount of 4-octylbenzenesulfonic acid adsorbed.

Curves A, B, and D of Fig. 6 shows the results obtained by Liu and Cantwell [15] for NBS^- on a column coated with tetrabutylammonium ion. The overall distribution coefficient, K_S, is calculated as follows:

$$K_S = K_{S,IEX} + K_{S,ADS} \quad (4)$$

where $K_{S,IEX}$ and $K_{S,ADS}$ are the contributions to the distribution coefficient from ion-exchange and adsorption processes. Curve C of Fig. 6 shows the distribution coefficient for ion exchange, $K_{S,IEX,R}$, corrected for potential variation in $K_{IEX,R}$ ob-

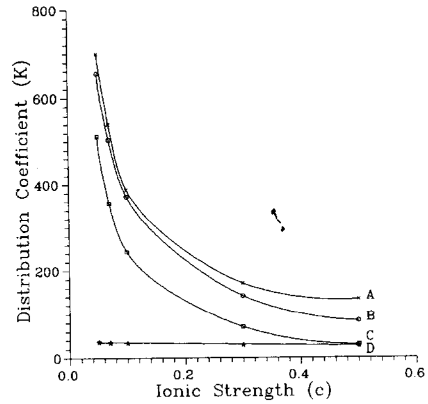

Fig. 6. Variation of distribution coefficient of NBS^- on octyldecylsilane packing with ionic strength. Experimental conditons: eluent, 0.010 *M* tetrabutylammonium chloride; Curves: A = K_S, B = $K_{S,IEX}$ (correced for variation in K_{IEX}), D = $K_{S,ADS}$ (Curve A, B and D from ref. 15).

served for inorganic cations. From Fig. 6 it is clear that the variations in $K_{IEX,R}$ do not effect the conclusions made by Liu and Cantwell [15] that ion exchange is the dominant process in the retention of the analyte, except at high ionic strengths where adsorption and ion-exchange distribution coefficients are of approximately the same magnitude. In addition, the changes in $K_{S,IEX,R}$ due to corrections for variation of $K_{IEX,R}$ with ion-exchange capacity for inorganic cations were determined to be more important at higher concentrations of surfactant in the mobile phase (higher loadings of surfactant).

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