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BEHAVIOR OF SIMPLE SALTS ON SILICA AND C₁₈ COLUMNS

RETENTION DYNAMICS OF CATIONS, ANIONS AND ION PAIRS

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SUMMARY

The retention behavior of simple inorganic salts on silica and ODS columns was investigated by high-performance liquid chromatography with methanol-water (80:20, v/v) as the mobile phase. Both a major (dissolved salt) and a minor (ion pair) peak were observed on the ODS columns; only the major peak was present on silica columns. The retention time of the major peak was a function of the number of moles of salt placed on the column and was sigmoidal with respect to the logarithm of the number of moles analyzed. The retention time of the minor peak was dependent upon the composition of the mobile phase. It disappeared in a mobile phase of water and was absent on a silica column. The general behavior was independent of the anion or cation being analyzed. The sigmoidal behavior of salt retention was attributed to both cationic and anionic exchange at the silica surface; the ion pair retention was attributed to solubility in the C₁₈ phase of the ODS columns. The areas under the major peak and the minor peak were used to calculate ion pair formation constants. For sodium nitrate, $K = 15 \cdot 10^{-3} M^{-1}$; for sodium nitrite, $K = 2.0 \cdot 10^{-3} M^{-1}$. The ion pair formation constants were used to calculate the theoretical distance of closest approach between the ions based on Bjerrum theory. For sodium nitrate, the distance calculated between center of Na⁺ and NO₃⁻ in the ion pair was 6.5 Å.

INTRODUCTION

Recently we used high-performance liquid chromatographic (HPLC) techniques to identify the reaction products formed in photoelectrochemical cells¹. The retention times of all known components of the reaction were determined on a Partisil ODS-2 column using methanol-water (80:20, v/v) as mobile phase at a flow-rate of 0.7 ml/min. During the identification procedure, a 25% difference in retention time between the reference sodium EDTA solution ($t_R = 3.45$ min) and the sample sodium EDTA solution from the reaction cell ($t_R = 4.35$ min) was observed. According to existing practice, sodium EDTA should have exhibited a constant t_R rather than the observed variation. This result was unexpected and suggested that perhaps sodium EDTA was retained on ODS columns and perhaps the common practice of measuring t_m by injection of a "non-retained" ionic species² should be reexamined.

In this study we have investigated the retention behavior of mono-charged salts on various ODS and silica columns. Systems peaks as well as anion peaks were observed in the absence of ion-pairing agents. The anion retention behavior is explained on the basis of competition between the cation and anion for active sites on the column. Finally, we suggest that the separation of two components, the dissolved solid and the ion pair, can be used to estimate ion pairing constants in the mobile phase.

EXPERIMENTAL

Materials

Reagent grade sodium salts were used. Methanol was HPLC grade and water was purified with a Milli-Q reagent grade water system.

HPLC systems

One HPLC apparatus consisted of a Perkin-Elmer Series 2/2 solvent delivery system equipped with a Rheodyne Model 7125 injection valve (20- μ l loop), a Model LC-75 variable-wavelength detector and an autocontroller. Recordings of chromatograms were made on a Hewlett-Packard Model 3390A computing integrator. The analytical columns used were 250 \times 4.6 mm I.D. Partisil 1025 ODS, ODS-2 and ODS-3. The columns were protected by a 70 \times 2.1 mm I.D. guard column containing Whatman CO: PELL ODS. The inorganic anions were detected at 205 nm. The flow-rate was 0.7 ml/min.

The second HPLC system consisted of a Perkin-Elmer Series 100 pump system equipped with a Rheodyne Model 7010 injector valve (10 μ l loop) and a Tri Det detector. Recordings of the chromatograms were made on a Series 5000 Fisher Recordall. The column used was a 3 \times 3 Perkin-Elmer HC-3 C₁₈ column.

The third system consisted of a Dionex Series 4000i system equipped with a 50- μ l loop, conductivity detector and Dionex anion and cation micro-membrane suppressors. Recordings of the chromatograms and data handling were made using both a Spectra-Physics SP 4290 integrator and an Epson Equity +1 computer equipped with a Spectra-Physics Labnet software program. The columns used were HPIC-AS4A analytical with a HPIC-AG4A guard for the anions and a HPIC-CS3 with a HPIC-CG3 guard for the cations (all the columns from Dionex).

Solution conductivities were obtained in methanol-water (80:20, v/v) at 25° \pm 0.1°C with a Model RC-18A Beckman conductivity bridge. The temperature was controlled with a Haake FK-2 constant-temperature bath.

The concentrations of the sodium and nitrate ions were obtained in the following manner. First, the appropriate sample, mobile phase or sample peak, was collected in an inert plastic syringe from the effluent of the Perkin-Elmer Series 2 HPLC system. The size of the peak samples ranged in size from 0.5 to 0.7 ml. The concentration of sodium and nitrate in the various samples was then measured by injecting the samples into the Dionex ion chromatography system.

RESULTS

Retention behavior of simple salts

The retention behavior studies were carried out using Partisil 1025 ODS, ODS-2 and ODS-3 reversed-phase columns and a silica A normal phase column. The specifics of these columns are shown in Table I. The general behavior on the three ODS columns is illustrated in Fig. 1. The sodium salts used in this study contained iodate, iodide, nitrite and bromide anions and the mobile phase was methanol-water (80:20, v/v). As shown in Fig. 1, the retention times of the salts on various reversed-phase ODS columns were a function of the number of moles injected onto the column. Furthermore, there was up to a 60% increase in retention time over the range $2 \cdot 10^{-9}$ – $9 \cdot 10^{-6}$ mol. This behavior was independent of carbon loading, available silanol sites and whether the column was capped or uncapped. Some additional features shown in Fig. 1 are: (1) retention times of the simple salts follow a pattern grouping themselves about a line characteristic of each column; (2) in the 10^{-9} – 10^{-8} mol region, the retention times on various ODS columns were fairly constant, but different for each one; (3) in the $5 \cdot 10^{-8}$ – $1 \cdot 10^{-6}$ mol region, a more linear increase in retention time occurred; (4) for quantities greater than 10^{-6} mol, retention times became fairly constant which could be attributed to saturation of the column since, at this point, tailing of peaks started to occur; (5) the scatter of points for each column, especially at higher number of moles, is probably due to variations in the atomic configurations of the monovalent anions injected onto the column; and (6) the retention behavior on each column appears to be relatively independent of the salt used.

TABLE I

WHATMAN PARTISIL 1025* AND PERKIN ELMER SILICA A** COLUMN SPECIFICATIONS

Whatman columns	Carbon loading (%)	Available silanols*** (%)
ODS	5	50
ODS-2	15	25
ODS-3	10	≈0.5 [§]

* Physical properties: irregular shaped; particle size, 10 μ m; surface area, 350 m²/g; pore volume, 0.85 ml/g; pore diameter, 85 Å.

** Physical properties: irregular shaped, particle size 10 μ m; pore diameter, 60 Å.

*** Available silanols refers to SiOH groups on the end of the C₁₈ chain attached to the surface of the silica beads.

[§] "Capped" column: available silanols on end of C₁₈ chain were converted to –SiOCH₃ groups.

Retention behavior of sodium nitrate

Sodium nitrate is recognized as a strong electrolyte and devoid of acid-base properties. Hence, it was chosen as a standard for documenting the general salt behavior observed above. Careful studies on ODS columns revealed that in addition to a major component, a minor peak for sample salts was present at longer retention

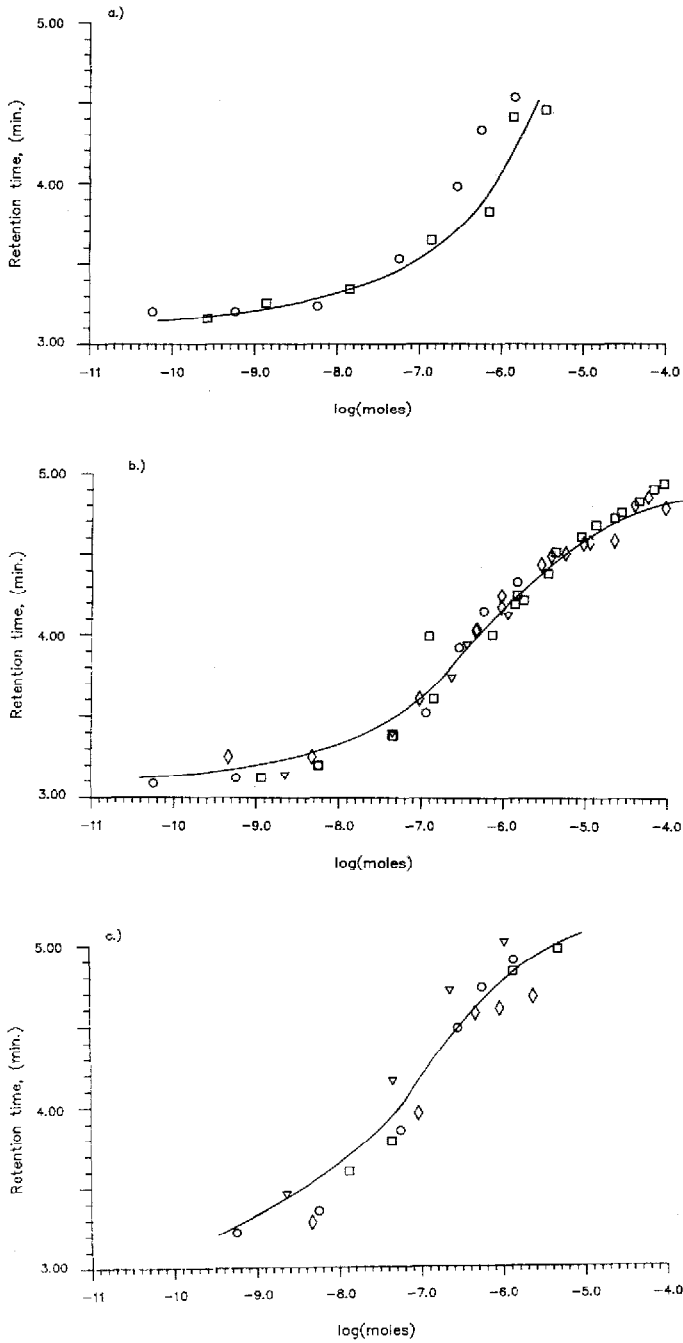


Fig. 1. Retention times (min) for sodium iodate (∇), sodium iodide (\circ), sodium nitrite (\square), sodium bromide (\diamond), as a function of the logarithm of the number of moles of salt on ODS (a), ODS-2 (b) and ODS-3 (c). The mobile phase was methanol-water (80:20, v/v) (pH 7). The flow-rate was 0.7 ml/min, $T = 20 \pm 2^\circ\text{C}$.

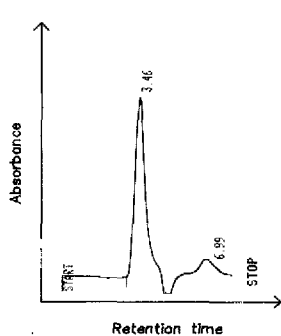


Fig. 2. Chromatogram of sodium nitrate showing the major peak (3.48 min) and the minor peak (6.96 min) on an ODS-2 column. The mobile phase of methanol-water (80:20, v/v) at a pH 6.3 and a flow-rate of 0.7 ml/min. The peak below baseline is a systems peak. These have recently been described in ref. 7.

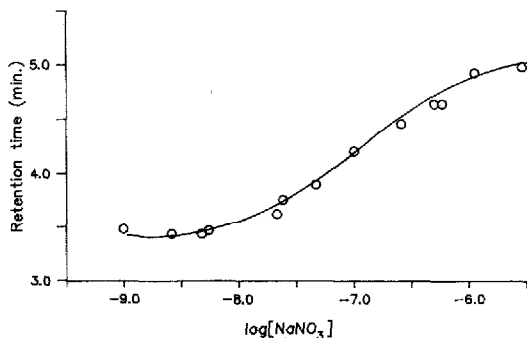


Fig. 3. Retention time (min) for sodium nitrate as a function of the logarithm of the number of moles of sodium nitrate injected, onto an ODS-2 column. The mobile phase was methanol-water (80:20, v/v) (pH 6.8) and the flow-rate was 0.7 ml/min.

times. This is shown in Fig. 2 for sodium nitrate. The retention behavior on an ODS-2 column of the major peak as a function of column loading is shown graphically in Fig. 3.

Effect of sample concentration

Variations in retention time were studied as a function of sample concentration. Samples of 20 μ l containing various concentrations of sodium nitrate were injected onto an ODS-2 column. According to the data in Table II, the retention time of the major peak decreased as the concentration decreased while the retention time of the minor peak remained constant. This data could be interpreted to mean that the retention time depended on concentration. However, the final column in Table II indicates that 2- μ l injections of solutions of differing molarity gave the same retention time as those in column one. Thus, the resulting retention times correspond to those based on the total number of moles of sodium nitrate injected onto the column.

TABLE II

RETENTION TIMES OF SODIUM NITRATE AT VARIOUS CONCENTRATIONS

Sodium nitrate concentration (M)	Retention time (min)*		Retention time (min)**
	Major peak	Minor peak	Major peak
$1 \cdot 10^{-4}$	3.27	6.8	3.41***
$1 \cdot 10^{-3}$	3.62	6.9	3.65 [§]
$1 \cdot 10^{-2}$	4.34	6.9	4.45 ^{§§}

* Column: Partisil ODS-2; mobile phase, methanol-water (80:20, v/v) at a flow-rate of 0.7 ml/min, pH 6.8; sample size 20 μ l; detection 205 nm.

** Retention time from Fig. 3 based on the number of moles of sodium nitrate in the sample.

*** 2 μ l injection of 0.0010 M sodium nitrate.

§ 2 μ l injection of 0.010 M sodium nitrate.

§§ 2 μ l injection of 0.10 M sodium nitrate.

TABLE III

RETENTION TIME OF SODIUM NITRATE (0.0100 *M*): DEPENDENCE ON AMOUNT

Column: Partisil ODS-2; mobile phase, methanol-water (80:20, v/v) at a flow-rate of 0.7 ml/min, pH 6.8.

Sample size (μ l)	Retention time (min)		Approximate area ratio
	Major peak	Minor peak	
10.0	4.15	6.81	300:1
5.0	3.95	6.85	100:1
0.5	3.58	6.88	32:1
0.1	3.38	6.91	6:1

Sample size

The injection volume was varied and the other parameters were held constant. The data in Table III indicate that the retention time of the minor peak remained constant while the retention time of the major peak decreased as the sample size decreased.

Mobile phase polarity

The polarity of the mobile phase was changed by altering the mole fraction of methanol-water from zero to one. According to the data in Table IV, the retention time of the minor peak tripled as the mole fraction of water in the mobile phase increased. In addition, the area ratio of the major to the minor peak increased as the mole fraction of water in the mobile phase increased and eventually at high levels of water the minor peak disappeared.

TABLE IV

RETENTION TIME OF SODIUM NITRATE IN VARIOUS METHANOL-WATER MOBILE PHASES

Column: Partisil ODS-2; flow-rate 0.7 ml/min, pH 6.8; sample size $4 \cdot 10^{-7}$ *M*.

Methanol (%)	Retention time (min)		Approximate area ratios
	Major peak	Minor peak	
100	4.00	4.97	40:1
90	4.07	5.23	30:1
80	4.13	5.55	45:1
60	4.14	7.48	50:1
40	4.12	10.58	50:1
20	4.17	14.14	100:1
0	4.14	—	—

Quantitative assessment of the sodium and nitrate-minor peak

The results of nineteen measurements on the concentration of the nitrate ion in the minor peak gave an average value of $1.858 \cdot 10^{-9} M$, $\sigma = 2.831 \cdot 10^{-10}$. An average of six measurements on the sodium concentration resulted in an average value of $2.475 \cdot 10^{-9} M$, $\sigma = 5.77 \cdot 10^{-10}$. These results indicate a sodium-to-nitrate ratio of approximately one to one was found in the minor peak region.

The content of sodium and nitrate in the mobile phase assessed between the major and minor peaks was $1.843 \cdot 10^{-9} M$, $\sigma = 1.64 \cdot 10^{-10}$, for sodium and below the detection limit for nitrate. Clearly, the minor peaks components are significant compared to the background.

TABLE V

RETENTION TIMES OF TBAN AND SODIUM NITRATE ON AN ODS-2 COLUMN

Mobile phase, methanol-water (80:20, v/v), flow-rate was 0.7 ml/min, pH = 6.9.

Moles	t_R (TBAN) (min)	t_R (sodium nitrate) (min)
$1 \cdot 10^{-9}$	3.38	3.42
$5 \cdot 10^{-9}$	3.38	3.44
$5 \cdot 10^{-8}$	3.64	3.88
$1 \cdot 10^{-7}$	3.98	4.23
$5 \cdot 10^{-7}$	4.37	4.69
$1 \cdot 10^{-6}$	4.63	4.89

Comparison of cations

The retention times of the major peaks of sodium nitrate on an ODS-2 column are compared to those of *tert.*-butylammonium nitrate (TBAN) on the same column in Table V. The retention times of sodium nitrate were slightly longer than those of TBAN, but both followed the same trend of a slight increase in retention time as the column sample loading increased.

The retention times for both salts were also determined on a silica column as a function of pH after adjusting the mobile phase with a small amount of 11.6 M perchloric acid. At low pH (2.7), the retention times for TBAN and sodium nitrate were nearly constant as given in Table VI. At a pH 4.9 and 6.3, TBAN followed the same trend observed for sodium nitrate. However, the retention time change was about a factor of 2 greater for TBAN than for sodium nitrate. In addition, the retention times of TBAN and sodium nitrate are reversed; now TBAN is retained by the column longer than sodium nitrate.

Systems peaks

Systems peaks were observed for samples containing methanol-water ratios other than 80:20 (v/v). These peaks were observed between the injection peak and the minor peak. The peaks were in the positive direction for greater methanol content

TABLE VI

RETENTION TIME OF TBAN AND SODIUM NITRATE ON A SILICA COLUMN AT VARIOUS MOBILE PHASE pH VALUES

Mobile phase, methanol-water (80:20, v/v), flow-rate was 0.7 ml/min.

Moles	TBAN			Sodium nitrate		
	pH 6.3	pH 4.9	pH 2.7	pH 6.3	pH 4.9	pH 2.7
$1 \cdot 10^{-9}$	3.91	3.72	5.81	3.47	3.37	6.23
$5 \cdot 10^{-9}$	4.10	3.83	6.06	3.44	3.56	6.23
$5 \cdot 10^{-8}$	4.91	4.51	6.06	3.88	3.85	6.23
$1 \cdot 10^{-7}$	5.01	4.96	6.03	4.23	4.06	6.14
$5 \cdot 10^{-7}$	5.75	5.75	6.27	4.67	4.57	6.23
$1 \cdot 10^{-6}$	5.85	6.07	6.11	4.89	4.56	—

(higher absorbance) and in the negative direction for greater water content (lower absorbance).

Conductivity detection

In all the previous studies, the mobile phase was monitored with a UV-VIS detector. The generality of the results was verified with a different instrument and a different detector. Both TBAN and sodium nitrate samples were injected onto a Perkin-Elmer HS-3, C₁₈, 3 × 3, ODS column and eluted with a methanol-water (80:20, v/v) mobile phase. A major peak eluted after 0.60 min for both salts; a minor peak eluted after 2.40 min for a sodium nitrate sample and after 2.54 min for a TBAN sample. The ratio of the major component to the minor component was 29:1 for the TBAN sample and 86:1 for the sodium nitrate experiment.

Dilution conductivity

Dilution conductivity studies were effected according to the procedures of Boggess and Zatko³. In water, sodium nitrate was completely dissociated in the 10^{-4} – 10^{-1} M range. However, as shown in Figs. 4 and 5, both sodium nitrate and TBAN give non-linear equivalent conductance plots indicative of ion pairs in methanol-water (80:20, v/v). This is expected in solvents of low dielectric constants.

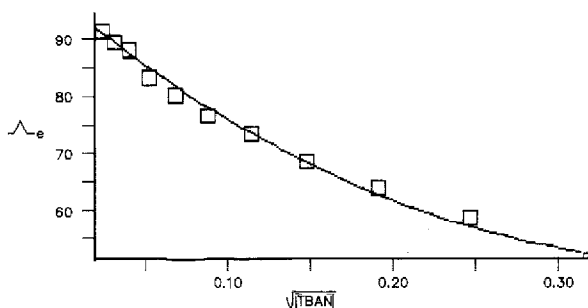


Fig. 4. Dilution conductivity profile for TBAN in methanol-water (80:20, v/v). $T = 25.0 \pm 0.1^\circ\text{C}$.

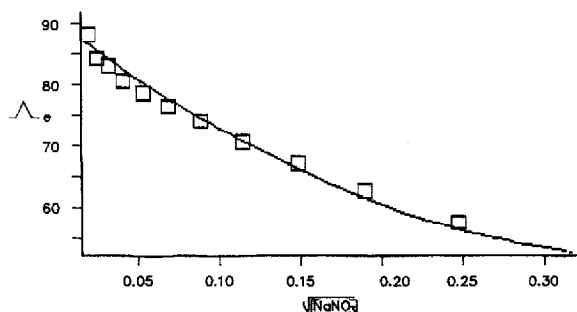


Fig. 5. Dilution conductivity profile for sodium nitrate in methanol-water (80:20, v/v). $T = 25.0 \pm 0.1^\circ\text{C}$.

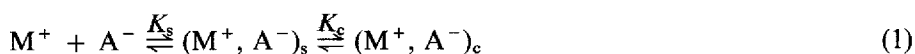
Solomon and Uchiyama⁴ recently reported formation constants for ion doublets and triplets in solvents of low dielectric constants ranging from 3 to 10. The ion pairing constants reported by Solomon and Uchiyama were large, ranging from 10^4 to $10^{11} M^{-1}$.

DISCUSSION

The experimental observations can be summarized as follows: (1) both a major and a minor peak were observed; (2) the major peak has the shorter retention time, the minor peak the longer one; (3) the retention time of the major peak changed as the number of moles of simple salt injected onto the column increased; (4) the retention time of the major peak remained constant as the composition of the mobile phase was varied; (5) simple salts behave similarly on the same column; (6) a comparison of the columns, silica, ODS, ODS-2 and ODS-3 indicates that the retention behavior of simple salts follows the same trend, but retention times differ somewhat for different columns; (7) the retention time of the minor peak increased as the water composition of the mobile phase increased and disappeared after the water fraction increased to one; (8) dilution conductivity indicates that simple salts are ion paired in methanol-water (80:20, v/v); (9) systems peaks derived from the solvent were observed when the sample injected onto the column was in a solvent other than methanol-water (80:20, v/v); (10) both sodium and nitrate were observed in the minor peak in a 1:1 molar ratio.

Systems peaks in this study were expected. They are reported to appear in liquid chromatograms when the mobile phase contains more than one component⁵ and the sample is dissolved in a solution different from the mobile phase^{6,7}. The systems peaks observed here meet this requirement. A positive peak at $t_R = 5.1$ min is observed for samples in more concentrated methanol and a negative peak is observed at $t_R = 4.7$ min for samples containing greater water content than the methanol-water (80:20, v/v) ratio. Both of these peaks also meet another criterion for systems peaks, the areas are non-linear with respect to sample size.

The major and minor peaks, on the other hand, are linear with respect to sample size and their presence can be explained on the basis of eqn. 1,



where M^+ and A^- are the dissociated ions, $(M^+, A^-)_s$ is the ion pair in the mobile phase, $(M^+, A^-)_c$ is the ion pair on the column and K_s and K_c are the respective equilibrium constants. The major peak is associated with the dissociated salt, $M^+ + A^-$ and $(M^+, A^-)_s$; the minor peak is associated with the ion pair, $(M^+, A^-)_c$. The rationale for the assignment is as follows: dilution conductivity results in methanol-water (80:20, v/v) clearly indicate that the major species in solution is the dissociated salt, but ion pairs are also present. Thus, variation in the retention time of the major fraction as a function of column loading is related to either interaction of the dissociated cation or anion with the column. Neither the identity of the monocation, the identity of the monoanion, nor the type of column appear to play a significant role in altering the retention behavior of the major peak. The pH of the mobile phase, however, does alter the retention characteristics. At a pH of approximately 4, retention times of the major peak appear to approach an upper limit. In a separate experiment, it was found that 0.5 g silanol column material in 10 ml water lowered the pH from 6 to 4.8. This suggests that the column bears excess negative charge and perhaps behaves as a cation-exchange column. The increase in retention times as the pH is lowered, however, implies the opposite, namely, the column operates by an anion-exchange mechanism. The signoidal character of Figs. 1 and 3 suggests that at low salt concentrations the cation-exchange mechanism may predominate whereas at high salt concentrations, the anion-exchange process takes precedence.

The minor peak is associated with the ion pair. It appeared when samples were prepared with Milli-Q-Water, methanol or methanol-water and the mobile phase was methanol-water (80:20, v/v) but disappeared when the mobile phase was water. The source of the peak is believed to be the ion pair since the ion pair is present in methanol-water (80:20, v/v) but not in water as determined by dilution conductivity measurements. Ion pairs apparently are retained on the column via the equilibrium process given in eqn. 1.

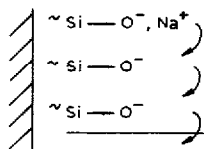
The mechanism most likely responsible for retention of the ion pair on the column is solubility of the ion pair in the C_{18} component of the ODS column. This is supported by the finding that the minor peak is absent on silica columns devoid of C_{18} linkages. The assignment of the minor peak to the ion pair is reasonable given that the retention time remains constant with column loading, but changes with mobile phase content variations. Clearly as the water fraction increases, the concentration of ion pairs decreases. Hence, the magnitude of the minor peak decreases. The reason for the increase in retention time as the water content of the mobile phase increases is related to the miscibility of water in the C_{18} phase of the column. There is an increase in the hydrophilic interaction of the mobile phase with the hydrophobic character of the C_{18} phase resulting in an increase in ion pair retention times as the water content of the mobile phase increases.

The mechanism

Silicon oxide surfaces have been studied in detail by others. The surface is acidic with a pK_a value of 7.1⁸. The acidity is derived from the silanol group on the surface as illustrated in eqn. 2.

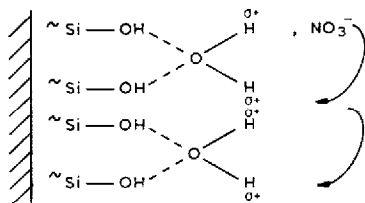


At high pH, the surface contains negatively charged groups which can behave as a cation-exchange column as illustrated in Scheme 1. According to Scheme 1, cations are retained on the column by SiO⁻ groups until they are eventually released from the column.



Scheme 1. A cation-exchange process observed on silica columns at low substrate concentration in methanol-water (80:20, v/v) (pH \approx 7).

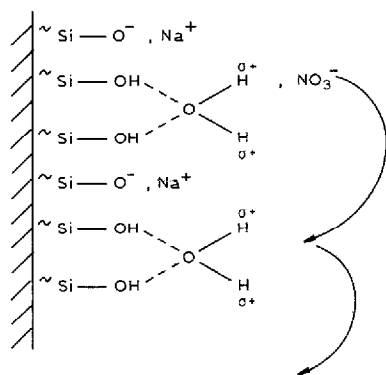
At lower pH (pH < 4), the acid sites are fully protonated. The surface would become neutral were it not for the fact that silica sorbs water⁹. The water is polarized and the partial positive end of the water molecule most likely interacts with substrates resulting in an anion-exchange column as illustrated in Scheme 2. According to this scheme, the anion is retained on the column by the water dipole until it eventually is released from the column.



Scheme 2. An anion-exchange process observed at pH < 4 on silica columns in methanol-water (80:20, v/v).

In addition, silica columns are known to adsorb cations in the order Cs⁺ > K⁺ > Na⁺ (ref. 10). The surface can then accommodate additional positive charge which is reflected in the retention time. For example, sodium nitrate has a longer retention time than TBAN as given in Table V. In this case, Na⁺ is preferentially sorbed onto the silica column and the retention time of sodium nitrate is slightly longer than for TBAN.

The mechanistic situation at pH > 4 and at higher substrate concentrations is a hybrid of both Schemes 1 and 2. At higher pH and greater column loading, two effects are important. The negative sites on the column become occupied by cations and adsorbed water polarizes the column as illustrated in Scheme 3. The predominant process under these conditions appears to be anion exchange as illustrated in Scheme 3, although cation exchange cannot be ruled out. Schemes 1 and 3 account for the sigmoidal character observed in Figs. 1 and 3. At low sample loading, the primary mechanism of retention is interaction of the cations with the negative column sites; at high loading, the primary mechanism for retention involves anion exchange via interaction of the anion with the positive dipole of the adsorbed water molecule.



Scheme 3. The anion-exchange process observed at $\text{pH} > 4$ with greater substrate loading on silica columns in methanol-water (80:20, v/v).

The mechanism of retention on silica and C_{18} derivatized silica columns without an ion pairing agent present in the mobile phase is more complex than the situation where an ion pairing agent is present. In the latter case, the cation is generally a large organic molecule which is soluble in the C_{18} phase of the column and acts as a site for anion exchange¹¹. Without the ion pairing agent present in the mobile phase, our results suggest that ion pairs of the original salt absorb into the C_{18} phase and are retained on the column longer than the cationic or anionic component.

Ion pairing constant determination

The area under the minor peak was taken to be indicative of the ion paired concentration; the area under the major peak was equated with the concentration of the dissociated salt. This was derived mathematically as follows:

$$\frac{(\text{area})_c}{(\text{area})_s} = \frac{(\text{M}^+, \text{A}^-)_c}{\text{A}_s^- + (\text{M}^+, \text{A}^-)_s} \approx \frac{(\text{M}, \text{A}^-)_c}{\text{A}_s} \quad (3)$$

The area of the minor peak is given by the ion pair eluted from the column $(\text{area})_c$; the area of the major peak is given by the sum of the anion and ion pair in the mobile phase $(\text{area})_s$, since the anionic component in its various forms is the species detected in the experiment. Ion pairing constants in polar solvents generally are on the order of 10^{-3} M^{-1} (see below) which means $\text{A}^- \gg (\text{M}^+, \text{A}^-)_s$ allowing eqn. 3 to be approximated as indicated.

Ion pairing constants can then be determined by eqn. 4 in the limit with $K_c = 1$.

$$K_s = \frac{[\text{M}^+, \text{A}^-]_s}{[\text{M}^+]_s[\text{A}^-]_s} = \frac{K_c[\text{M}^+, \text{A}^-]_c}{[\text{M}^+]_s[\text{A}^-]_s} \approx \frac{[\text{M}^+, \text{A}^-]_c}{[\text{M}^+]_s[\text{A}^-]_s} \approx \frac{(\text{area } \text{M}^+, \text{A}^-)_c}{(\text{area, } \text{A}^-)_s^2} \quad (4)$$

The ion pair association constant determined for an average of four samples for sodium nitrate was $15 \cdot 10^{-3} \text{ M}^{-1}$ and for sodium nitrite was $2.0 \cdot 10^{-3} \text{ M}^{-1}$ under similar conditions.

Fuoss and Krauss¹² reported an ion pairing constant of $2.9 \cdot 10^{-3} M^{-1}$ for sodium nitrate in liquid ammonia at -40°C . The ion pair formation constant they found for tetraisoamylammonium nitrate in a dioxane-water (47:53, v/v) system was $0.15 M^{-1}$. The dielectric constant of this solvent mixture was 38, close to 41 for the methanol-water (80:20, v/v) mixture used in our studies.

The distance of ion separation in the ion pair was estimated using Bjerrum theory¹³ of ionic association. The theory relates the ion pair formation constant to electrostatic, solvent, and distance of charge separation parameters¹⁴. Substitution of the appropriate parameters for sodium nitrate in methanol-water (80:20, v/v) at 20°C resulted in a distance of charge separation between the centers of sodium and nitrate of 6.7 Å. This value certainly is reasonable given that the ionic radius of sodium is 1.16 Å, nitrate is 1.65 Å (ref. 15) and the fact that the ions are solvated in solution.

The closeness of both experimental and theoretical ion pairing constants lend credibility to the assumption that $K_c \approx 1$.

CONCLUSIONS

This paper points out two important items. The first indicates that C₁₈ derivatized silica columns exhibit dual functionality. The silica backbone functions as an ion exchange resin; the C₁₈ component dissolves the ion pair. This allows the determination of ion pairing formation constants by a new method. The second item is related to equating t_m to t_R for simple anions on ODS columns. Clearly this is incorrect and a standard will need to be defined in order to report data for reproducibility. Sodium nitrate at low concentration ($< 10^{-8} M$) seems to be an excellent choice.

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