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## RETENTION OF SOME SIMPLE ORGANIC CATIONS ON AN ANION EXCHANGE COLUMN

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### ABSTRACT

The retention behavior of a homologous series of phenyl-substituted alkylammonium ions on a styrene-divinylbenzene copolymeric anion exchange column with acetonitrile - aqueous solution mobile phase was investigated. As the concentration of eluent anion increased, the retention of elute cation was increased. This relationship showed good linearity in log-log coordinates. The methylene selectivity of members of a homologous series of elute cations was also studied.

### INTRODUCTION

Ion exclusion chromatography has been used for the separation of ionic from non-ionic species (1), especially for the separation of weak organic acids with cation exchange resins in the hydrogen form (2-8). Ion

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exclusion separation is based on Donnan exclusion, i.e., electrostatic interaction between the elute and the charged functional groups in the stationary phase. When cations are introduced onto an anion exchange column, they pass quickly through the column and elute faster than neutral solutes because they are excluded from, or repelled by the positively charged resin surface because of its Donnan potential. Non-ionized solutes can penetrate the resin network and are retained by partition or other forces.

There are several factors which play a role in the retention process other than Donnan exclusion in ion exclusion chromatography. These are sorption on the surface of the matrix of the ion exchange resin (1,7-9), size (steric) exclusion (6-7,10), hydrophobic interaction (5-6), and hydrogen bonding (5). Many experimental conditions contribute to the retention of elutes in ion exclusion. These include the temperature (11), pH of mobile phase (12-13), and ionic strength of eluent (12-14).

In this paper, the retention behavior of a homologous series of phenylalkylamines on a styrene-divinylbenzene copolymeric anion exchanger was investigated. The effect of eluent ion concentration on the retention of elutes under conditions of ion exclusion chromatography was observed. A homologous series of elutes was chosen to evaluate solvophobicity on retention. Benzyl alcohol was chosen to investigate the dependence of a nonionized solute on eluent ion concentration.

## EXPERIMENTAL

### Equipment

The liquid chromatograph consisted of a Waters M-6000A solvent delivery pump (Waters Associates, Milford, MA), a Rheodyne model 7125 injector (Cotati, CA) with a 200  $\mu$ L sample loop (Alltech Associ-

ates, Deerfield, IL), a Kratos Spectroflow 773 variable wavelength UV-VIS detector (Ramsey, NJ), and a Houston Instrument model 4511 strip chart recorder (Austin, TX). A Hamilton PRP-X100 column (150 x 4.1 mm) (Hamilton, Reno, NV) packed with 10  $\mu\text{m}$ , spherical poly(styrene-divinylbenzene) trimethylammonium exchanger was used. To control the column temperature, a FIATron (Madison, WI) CH-30 column heater and TC-50 controller were used. The column was thermostated at the desired temperature for 1 hour prior to injection.

An Alltech solvent filtration kit and 0.45  $\mu\text{m}$  membrane filter were used to filter the eluent solutions. An Alltech series 6000 syringe filter (0.45  $\mu\text{m}$ ) and a 10 mL Luer-lox glass syringe (Curtin Matheson Scientific, Inc., Houston, TX) were used to filter the injection solvent. An Orion Research model 601 A/digital Ionalyzer (Orion Research, Inc., Boston, MA) was used to measure pH. The deionized water was prepared by using a Sybron-Barnstead 60209 water purification system (Boston, MA). An ultrasonic water bath (L&R Manufacturing Industry, Kearny, NJ) was used to degas the mobile phases.

### Reagents

Benzyl alcohol was analytical grade and was obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ). Benzylamine, 2-phenylethylamine, 3-phenyl-1-propylamine, and 4-phenyl-1-butylamine were of 98%+ purity and were purchased from Aldrich Chemical Co. (Milwaukee, WI). Sodium nitrate and sodium chloride were ACS grade and were obtained from Fisher Scientific Co. (Fair Lawn, NJ). Sodium bromide was Mallinckrodt (St. Louis, MO) analytical-reagent grade. Hydrochloric acid was ACS grade and was purchased from Curtin Matheson Scientific, Inc. (Houston, TX). Acetonitrile was HPLC grade and was also obtained from Curtin Matheson Scientific, Inc.

### Chromatographic Conditions

The mobile phase flow rate was 1.0 mL/min. The detector wavelength was set at 254 nm with sensitivity 0.005 AUFS. The injection volume was 10  $\mu$ L. To inject the eluate a Hamilton 50  $\mu$ L microsyringe was used. The eluate solution was injected three times and average values of  $k'$  were calculated. To determine  $t_0$ , 5-10  $\mu$ L of deionized water was injected. The column temperature was controlled at 35°C.

### Procedure

In a typical procedure, the necessary amount of sodium nitrate to produce the desired eluent anion concentration was weighed into a 500 mL volumetric flask. A volume of 5 mL of 0.1 M HCl solution was added to it to get the desired pH (pH = 3.0). The solid was dissolved and the solution was made up to 500 mL by adding deionized water. Then the solution was filtered with a 0.45  $\mu$ m membrane filter. From this solution the necessary volume was taken to prepare the mobile phase. The mobile phase was prepared by mixing 10 volume % of acetonitrile with 90 volume % of nitrate anion solution. Bromide and chloride ion solutions were prepared in the same way. Eluent anion concentrations ranged from 30 to 300 mM in the aqueous solution prior to mixing with acetonitrile. The change in volume on mixing was assumed insignificant. After mixing the mobile phase was degassed with an ultrasonic bath.

In a typical procedure for preparing eluate solution, 20  $\mu$ L of benzylamine was dissolved in 1 mL of acetonitrile, and 5  $\mu$ L of this stock solution was taken and diluted to 2 mL with mobile phase, and the mixture was vortex mixed for 10 s.

## RESULTS AND DISCUSSION

The pH of the eluent solution was adjusted to pH = 3.0, where the phenylalkylamines used as eluates remained in their ammonium cation

form. It was expected that all the cations would be repelled by the ammonium group on the column resin, thus showing short retention times. Indeed, short retention occurred when the mobile phase had no eluent ion added except 1mM H<sup>+</sup> and 1mM Cl<sup>-</sup> to keep the pH 3.0 even though the mobile phase was 90 % water and only 10 % acetonitrile. All the phenylalkylammonium ions eluted earlier than deionized water. Retention volumes less than the void volume ( $v_0$ ) were attributed to the elutes' inability to occupy all of the volume used by the deionized water because of the repulsion between elute ion and the resin functional group (15).

When inorganic ions were added to the mobile phase, the retention volumes of the phenylalkylamines increased. Figure 1 shows the linear relationship between the log of the capacity factors of benzylammonium, 2-phenylethylammonium, 3-phenyl-1-propylammonium, and 4-phenyl-1-butylammonium ions and the log of the concentration of nitrate ion in the aqueous fraction of mobile phase. Similar curves were obtained with bromide and chloride eluent anions.

The retention of phenylalkylammonium ions increased with an increase in the salt concentration from 30 to 300 mM. Similar dependencies were observed in earlier studies. Slais (14) observed an increase in  $k'$  of aromatic acid anions as the concentration of ammonium sulfate in the mobile phase increased. Jandera et al (16) showed that the retention of aromatic sulfonic and carboxylic acids on a reversed phase column was increased by adding strong electrolytes to the mobile phase in the absence of an ion pair forming substance. The retention volume increased in the order of the size of the anion or cation used in the mobile phase. They also found linear relationships between the concentration of Na<sub>2</sub>SO<sub>4</sub> and the  $k'$  of aromatic sulfonic acids in log-log coordinates. They obtained the empirical equation that describes the influence of salt concentration,  $c$ , on the capacity factor,  $k'$ :  $\ln k' = A +$

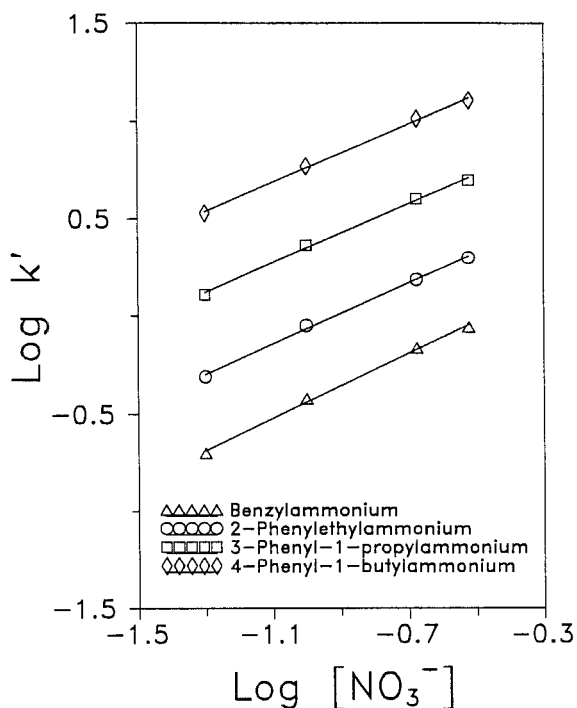


FIGURE 1. Relationship between the log of the capacity factor of phenylalkylammonium ions and the log of nitrate ion concentration in the aqueous fraction of the mobile phase.

B In c, where A and B are constants depending on the elute, eluent salt, solvent and column used. An explanation of the meaning of these constants was not given. The linear relationship between  $\log k'$  of phenylalkylammonium elutes and the log of the concentration of salt was consistent with the empirical equation obtained by Jandera et al (16).

These results for the phenylalkylammonium elutes were similar to ion pair reversed phase liquid chromatography results although a hydrophobic ion pairing reagent was not added. The reversible formation

of an ion pair between eluent anion and elute cation is a possible interpretation of these results. As would be expected from an ion pairing equilibrium the  $k'$  of ammonium ions increased as the concentration of eluent anion increased.

The retention of phenylalkylammonium ions was also influenced by the kind of salt in the mobile phase. Figure 2 presents the  $\log k'$  of 4-phenyl-1-butylammonium ion as a function of the  $\log$  of eluent ion concentration in the mobile phase. The  $k'$  of 4-phenyl-1-butylammonium ion increased in the order  $\text{Cl}^- < \text{Br}^- < \text{NO}_3^-$ . The order is related to the ion exchange strength of the eluent ion (17), i.e., the size of anion (18). This result also can be interpreted in terms of ion pairing. As the size of the anion increased, pairing strengthened and solvophobic interaction between the ion pair and the mobile phase increased.

Another possible interpretation is that the eluent ion in its double layer produces a blocking effect. As the concentration of eluent ion increased, the accessible functional group volume is decreased because of the electrostatic interaction between eluent ion and the functional group of the anion exchange column. Therefore, the elute cation experienced less repulsion, and consequently longer retention. The blocking effect was in the order  $\text{NO}_3^- > \text{Br}^- > \text{Cl}^-$ . This is consistent with ion exchange strength, the interaction between eluent ion and functional group of the stationary phase (17).

There was an increase in retention of phenylalkylammonium ions as the carbon number in the alkyl group increased. This is again an example of a homologous series of elutes eluting in the order of increasing length of their aliphatic chains and it is attributed to sorption by the resin due to the solvophobicity of the organic ammonium ions.

Figure 3 depicts the plot of  $\log k'$  vs. carbon number of the alkyl group in the phenylalkylammonium cations for different inorganic eluent



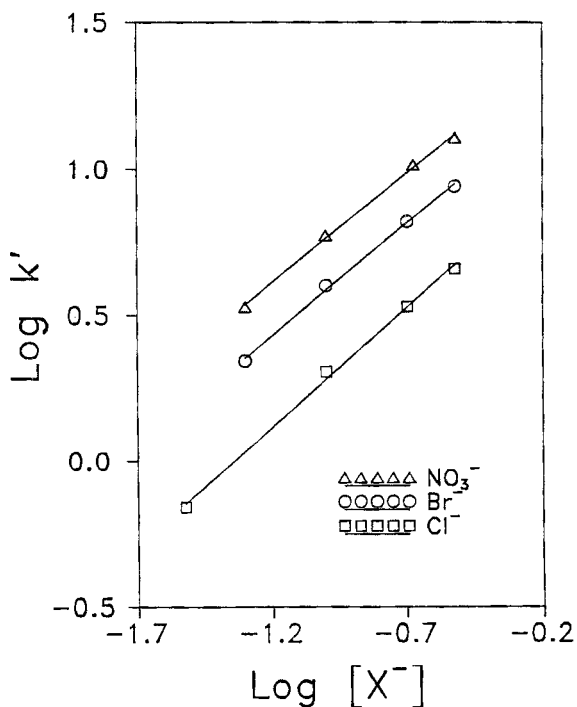


FIGURE 2. Relationship between the log of the capacity factor of 4-phenyl-1-butylammonium ion and the log of the inorganic ion concentration in the aqueous fraction of the mobile phase.

ions of 0.100 M concentration in the aqueous fraction of the mobile phase. The slope of this plot is  $\log \alpha_{\text{CH}_2}$ , where  $\alpha_{\text{CH}_2}$  is the selectivity between nearest homologous ammonium cations. At the 95% confidence level, these three lines are parallel. Thus, the selectivity was not affected by changing the type of eluent ion.

Figure 4 presents the relationship between  $\log k'$  and the carbon number of the alkyl group in phenylalkylammonium cations for different nitrate ion concentrations. The slope shows that this increase is

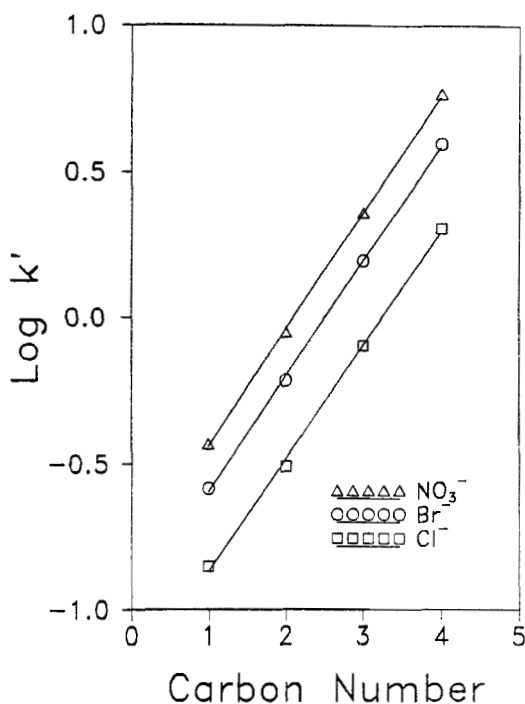


FIGURE 3. Relationship between the log of the capacity factor and the carbon number of the alkyl group in phenylalkylammonium ions with different inorganic eluent ions: 0.100 M of eluent ion in the aqueous fraction of the mobile phase.

systematic, and these three lines are parallel at the 95% confidence level. Thus, the selectivity between two homologous elutes was not affected by the concentration of the eluent ion. These results are consistent with those for phenylalkylcarboxylate anions in ion exchange chromatography (17).

Even though it is not shown, the retention of benzyl alcohol was little affected by the kind and concentration of eluent. As the concentration of eluent ion increased, the  $k'$  of benzyl alcohol increased a small,

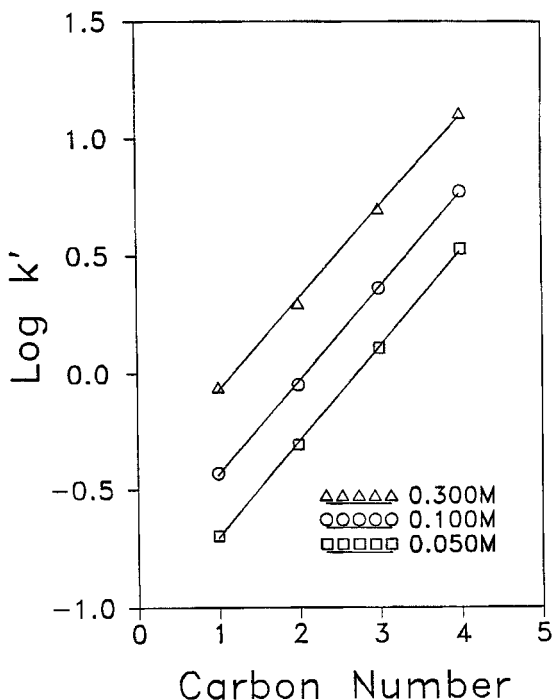


FIGURE 4. Relationship between the log of the capacity factor and the carbon number of the alkyl group in phenylalkylammonium ions with different nitrate ion concentrations in the aqueous fraction of the mobile phase.

almost insignificant, amount. This is thought to be due to salting out (19).

### CONCLUSION

The retention of organic cations on an anion exchange column has been interpreted as being the result of a combination of ion exclusion and solvophobic interaction. As the eluent ion concentration increased, the retention of elute cations increased. The extent of retention

depended on the concentration and kind of inorganic eluent ion. However, the methylene selectivity among members of a homologous series of elute cations was not affected by the nature or concentration of eluent ion.

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