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## Cation-exchange chromatography in non-aqueous solvents

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### Abstract

Much of the selectivity of organic ions in conventional ion chromatography comes from hydrophobic interaction between the carbon chain of the analyte ions and the polymer matrix of the ion exchanger. By operating in organic solvents containing little, if any, water, the true ion-exchange selectivity of various organic ions can be measured. Retention factors (capacity factors,  $k'$ ) for a series of protonated amine cations were measured in methanol, ethanol, 2-propanol and acetonitrile using a polymeric cation-exchange resin, conductivity detection, and eluents of methanesulfonic acid in the same organic solvent. Plots of  $\log t'_R$  vs.  $\log$  methanesulfonic acid concentration were linear with slopes close to the theoretical slope of  $-1.0$  except for acetonitrile where the slopes averaged  $-0.82$ . The retention factor showed little change with increasing carbon chain length in  $n$ -alkylamine cations, but increased substantially at fixed eluent concentration in going from methanol, to ethanol, to 2-propanol and especially to acetonitrile.

Several practical separations of organic amine cations were demonstrated in non-aqueous media. One advantage of this technique is that neutral organic analytes elute very quickly in non-aqueous media and thus do not interfere with chromatographic separations of the ions.

### 1. Introduction

Organic solvents have been used extensively in classical ion-exchange chromatography to aid in the separation of metal cations [1–3]. Formation of metal complexes with chloride and other anions was found to occur much more readily in organic solvents than in water alone. Organic solvents have also been added to aqueous eluents in modern ion chromatography to modify the behavior of various ionic analytes. However, the percentage of organic solvent in the eluent has generally been  $< 20\%$ . Rabin and Stillian [4] recently discussed practical aspects on the use of organic solvents in ion chromatography (IC). The solvents were used primarily for selectivity

mediation of the ion-exchange process for separation of various anions.

In the IC separation of organic cations it has long been known, or at least suspected, that the mechanism involved more than simple ion exchange. Hoffman and co-workers [5,6] have shown that two mechanisms occur in such cases: ion exchange and hydrophobic interaction between the sample cations and the resin matrix. For example, these authors showed that the slopes of the linear plot of  $\log k'$  vs. carbon number for protonated amine cations decrease going from 30% acetonitrile (70% water) to 70% acetonitrile in the eluent. This is due to lower hydrophobic interaction in the 70% acetonitrile.

The purpose of the present investigation was to study IC in organic solvents containing little if any water. Under these conditions solvation of

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the lipophilic part of the cation should be sufficient to virtually eliminate the hydrophobic interaction between the sample cations and the resin. In this way the true ion-exchange selectivity can be measured. This paper deals with ion-exchange chromatography of organic cations in non-aqueous solvents. A companion paper is concerned with alkali-metal cations in organic solvents [7].

## 2. Experimental

### 2.1. Chromatographic system

The chromatographic system consisted of several components. An Alltech (Deerfield, IL, USA) 425 HPLC pump was used to deliver a flow of 1 ml/min. A 7125 Rheodyne (Berkeley, CA, USA) injector delivered a 10- $\mu$ l sample which was detected with a Alltech 320 conductivity detector. A Hitachi D-2000 integrator (EM Science, Cherry Hill, NJ, USA) was used to measure retention times. Separations were recorded by a Servogor 120 chart recorder (Abb Goerz Instruments, Vienna, Austria), and a Keithley Chrom 1-AT data acquisition board (Keithley MetraByte Corp., Taunton, MA, USA) with Labtech Notebook software (Laboratory Technologies Corp., Wilmington, MA, USA). Columns were packed with a Shandon Southern (Sewichley, PA, USA) HPLC packing pump at 3000 p.s.i. (1 p.s.i. = 6894.76 Pa).

### 2.2. Reagents and chemicals

The cation-exchange resin was prepared in our laboratory from 5- $\mu$ m macroporous polystyrene-divinylbenzene (Sarasep, Santa Clara, CA, USA). A 2-g amount of resin was slurried with a few milliliters glacial acetic acid. An excess of concentrated sulfuric acid was then added to the resin slurry and placed in an ice bath. This reaction mixture was stirred for 0.5 to 4 min to produce the desired exchange capacity of 0.15 or 0.65 mequiv./g. Methanol, acetonitrile and 2-propanol were of HPLC grade and used as obtained from Fisher Scientific (Pittsburgh, PA,

USA). Punctilious absolute ethanol was used as obtained from Quantum Chemicals (Newark, NJ, USA). All eluents were prepared daily. The analytes and methanesulfonic acid eluent were all of reagent grade and used as obtained from Lancaster Synthesis (Windham, NH, USA), Aldrich (Milwaukee, WI, USA), and Fisher Scientific. Stock solutions of 1000 ppm were used to prepare all samples.

## 3. Results and conclusions

### 3.1. Types of resin

One common resin used for separation of cations in modern IC is a sulfonated microporous resin of low exchange capacity [8,9] or a resin coated with a latex of low cross-linking. These materials tend to swell somewhat in water to form a gel. In the present study a sulfonated macroporous resin of high cross-linking was used. This resin is compatible with a wide variety of organic solvents and appears to undergo little if any swelling in going from one solvent to another.

### 3.2. Effect of eluent cation concentration

After trying several different inorganic acids, methanesulfonic acid was selected as the eluting acid for the separation of protonated amine cations. In IC of cations with  $H^+$  as the eluting cation,  $k'$  should vary according to the following equation:

$$\log k' = -m \log H^+ + b$$

where  $m$  is the slope of a linear plot and  $b$  is a constant. Linear plots were obtained for the  $C_1$ – $C_{10}$  *n*-alkylamines in methanol, ethanol, 2-propanol and acetonitrile. The slopes ( $m$ ) were very close to the theoretical slope of  $-1$  in the three alcohols and only a little less than  $-1$  in acetonitrile (Table 1).

### 3.3. Effect of solvent on $k'$

A plot of  $\log k'$  vs. the number of carbon atoms is linear for members of a homologous

Table 1  
Slopes of  $\log t'_R - \log [H^+]$  lines for several solvents

	Methanol	Ethanol	2-Propanol	Acetonitrile
Methylamine	-0.95	-1.02	-0.92	-0.85
Ethylamine	-0.94	-1.00	-0.92	-0.85
Propylamine	-0.93	-1.01	-0.93	-0.84
Butylamine	-0.93	-1.01	-0.92	-0.83
Pentylamine	-0.92	-1.00	-0.93	-0.81
Hexylamine	-0.90	-1.00	-0.93	-0.80
Heptylamine	-0.92	-1.00	-0.93	-0.78
Octylamine	-0.92	-1.01	-0.92	-0.79
Nonylamine	-0.90	-1.00	-0.92	-0.82
Decylamine	-0.89	-1.01	-0.92	-0.81

The resin contained 0.65 mmol/g of  $-\text{SO}_3\text{H}^+$ . Eluents contained 75, 50, 25 and 10 mM methanesulfonic acid.

series in HPLC [10]. The slope of such a plot is an indication of the extent of the hydrophobic effect of the carbon chain on the retention factor,  $k'$ .

The retention factors of  $\text{C}_1$ – $\text{C}_{10}$  *n*-alkylamine cations were measured under identical chromatographic conditions in each of four organic solvents. The results are shown graphically in Fig. 1. The values of  $k'$  are very similar for the various amines in any given solvent except in methanol, where a gradual increase is noted for  $k'$  with increasing carbon chain length. This could be interpreted as some residual hydrophobic attraction in methanol of the amine cations for the resin. The  $k'$  values for the homologous series increases in the order methanol < ethanol < propanol  $\ll$  acetonitrile.

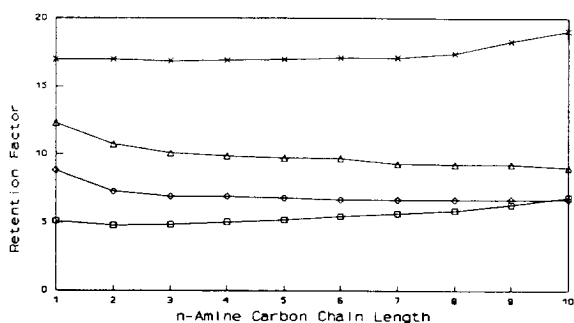


Fig. 1. Effect of solvent on retention of *n*-alkylamines. Eluent contained 25 mM methanesulfonic acid. The resin contained 0.65 mmol/g of  $-\text{SO}_3\text{H}^+$ . □ = Methanol; ◇ = ethanol; △ = 2-propanol; × = acetonitrile.

These results might be explained by a lower degree of solvation of the  $\text{RNH}_3^+$  in acetonitrile than in the alcohols where hydrogen bonding through the  $-\text{OH}$  is a possibility. A higher degree of solvation would attract the  $\text{RNH}_3^+$  more strongly to the liquid mobile phase and could impede the approach of a highly solvated ion to the ion-exchange sites on the resin.

The retention factors of a number of amine cations are given in Table 2. Elution is strongly dependent on solvation of the amine cation and the dielectric of the eluent. The effect of dielectric is seen by the 2-propanol  $k'$  values in Table 2. Although 2-propanol should be a stronger eluent for the amines, retention times are longer. This is due to the low dielectric constant of 2-propanol which favors the amine cation remaining paired to the resin exchange sites. Methanol and ethanol have more moderate dielectric constants but have different efficiencies for solvating straight-chain and aromatic amines as can be seen by the retention factors of the octyl and aniline cations.

### 3.4. Separation of protonated amine cations

The data in Fig. 2 indicate that none of the solvents studied would be a suitable choice for separation of the *n*-alkylamine ions. However, an excellent separation was obtained for the protonated cations of aniline, *N*-methylaniline and *N,N*-dimethylaniline (Fig. 2). These ions

Table 2  
Retention factors of protonated amine cations in alcohol solvents

Amine	Methanol	Ethanol	2-Propanol
Aniline	1.98	1.62	5.78
N-Methylaniline	3.18	4.10	13.64
N,N-Dimethylaniline	4.37	7.68	27.6
Octylamine	2.39	1.82	4.83
Dioctylamine	4.57	3.26	9.43
Trioctylamine	7.54	4.61	17.6

Conditions: 1 mM methanesulfonic acid, 5 cm column with 0.15 mmol/g of  $-\text{SO}_3^-\text{H}^+$ .

differ only by one or two methyl groups. Good separations were also obtained in methanol for a sample containing ethylamine, diethylamine and triethylamine and for another sample containing *n*-octylamine, di-*n*-octylamine and tri-*n*-octylamine (Fig. 3). A mixture of pyridine, quinoline and benzoquinoline could be separated in methanol or in mixed solvents containing 65% methanol and 35% of ethanol, propanol (Fig. 4) or butanol.

Conductivity detection can be used in any of the solvents studied but the sensitivity is better in eluents with higher dielectric constants (methanol and acetonitrile). Elution of an amine cation reduces the concentration of the more mobile  $\text{H}^+$  and thereby gives a peak of decreased conductance for the alcohol solvents. Conversely,  $\text{H}^+$  has a lower conductivity than the amine cations in acetonitrile and a positive signal was measured. For convenience, the chromatograph-

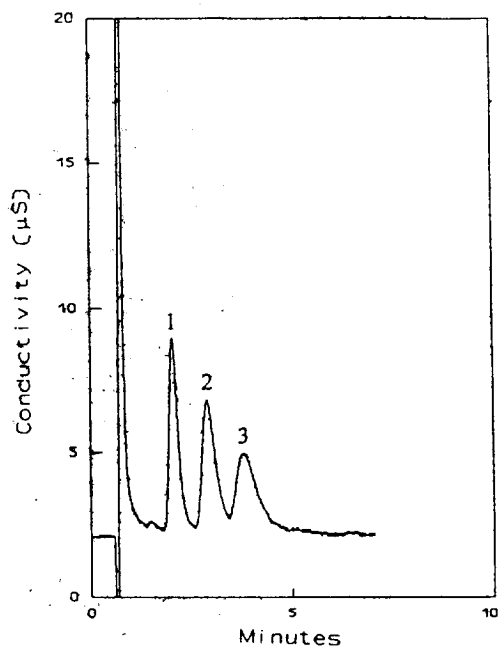


Fig. 2. Separation of 12.5 ppm aniline (1), N-methylaniline (2) and N,N-dimethylaniline (3) on a 5-cm sulfonated resin column (0.15 mmol/g). The eluent was 1 mM methanesulfonic acid in methanol at a flow-rate of 1 ml/min.

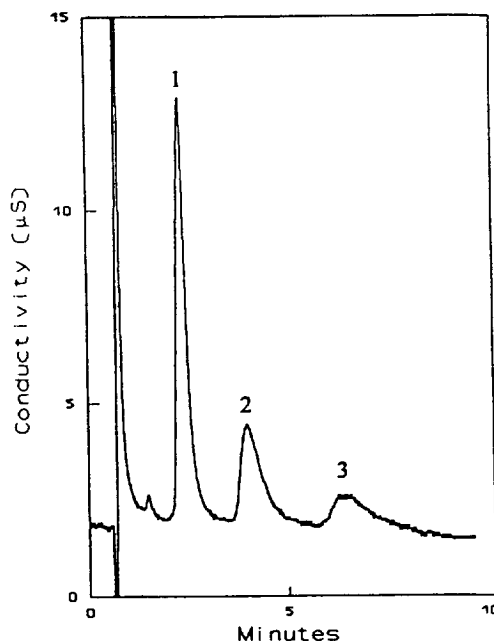


Fig. 3. Separation of 50 ppm *n*-octylamine (1), di-*n*-octylamine (2) and tri-*n*-octylamine (3) in methanol. Conditions as in Fig. 2.

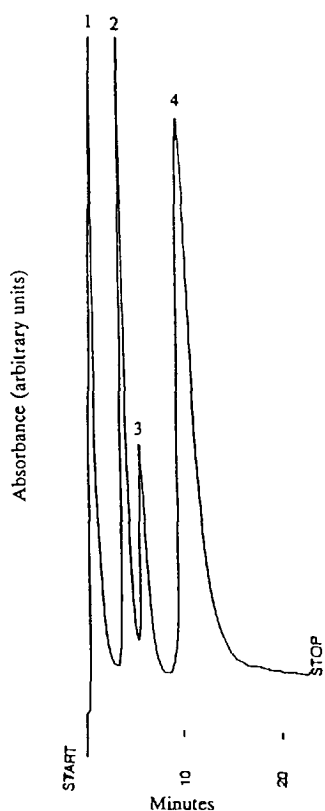


Fig. 4. Separation of 0.4 ppm pyridine, 40 ppm quinoline and 60 ppm 5,6-benzoquinoline in a sample also containing 2000 ppm each of benzonitrile, nitrobenzene, octane and isophorone. The solvent was methanol-*n*-propanol (65:35). Peaks: 1 = 2000 ppm each of benzonitrile, octane, nitrobenzene, isophorone (collect fraction and GC: 100, 95, 92 and 100% recoveries, respectively); 2 = pyridine; 3 = quinoline; 4 = 5,6-benzoquinoline.

ic peaks are displayed graphically on a conventional *y*-axis of increasing signal.

The retention factors of most neutral organic compounds are very low in the solvents studied. This means that neutral organic compounds will be eluted quickly enough not to interfere with chromatographic separation of the amine cations. Fig. 4 shows a successful separation of 0.4 ppm pyridine, 40 ppm quinoline and 60 ppm of 5,6-benzoquinoline in a sample that also contained 2000 ppm each of benzonitrile, *n*-octane, nitrobenzene and isophorone. The neutral fraction was collected and analyzed by gas chromatography giving recoveries of 100, 95, 92 and

100%, respectively for the four neutral compounds.

Separation of 50 ppm each of aniline, *N*-methylaniline and *N,N*-dimethylaniline in a sample spiked with 10 000 ppm of toluene is shown in Fig. 5. The toluene elutes in a very compact, early peak.

### 3.5. Determination of trace amines in organic solvents

With the use of organic eluents, it should be possible to detect very small amounts of organic bases in solvents. A large volume of organic solvent may be injected. The amine will be retained by electrostatic attraction while the solvent passes through the column with the injection peak. In Fig. 6, 50 ppb aniline in toluene (with 0.75 mM methanesulfonic acid) is determined. The detection limit of this system was determined by analyzing the baseline noise after the elution of the aniline peak. Using three times the standard deviation of the signal noise

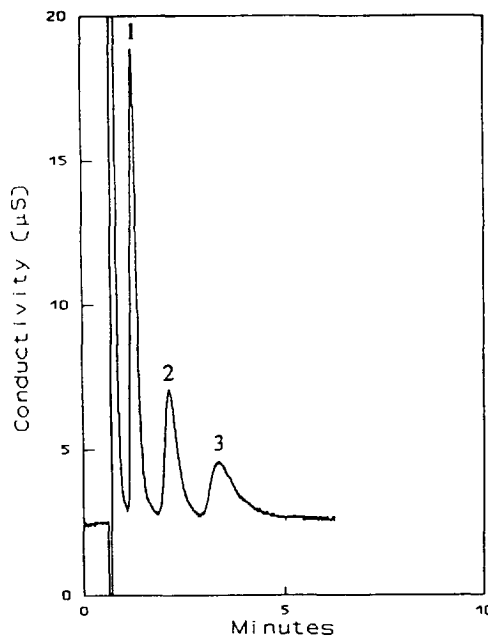


Fig. 5. Separation of 50 ppm aniline (1), *N*-methylaniline (2) and *N,N*-dimethylaniline (3) in a sample spiked with 10 000 ppm toluene. The eluent was 2.5 mM methanesulfonic acid in ethanol. Other conditions as in Fig. 2.

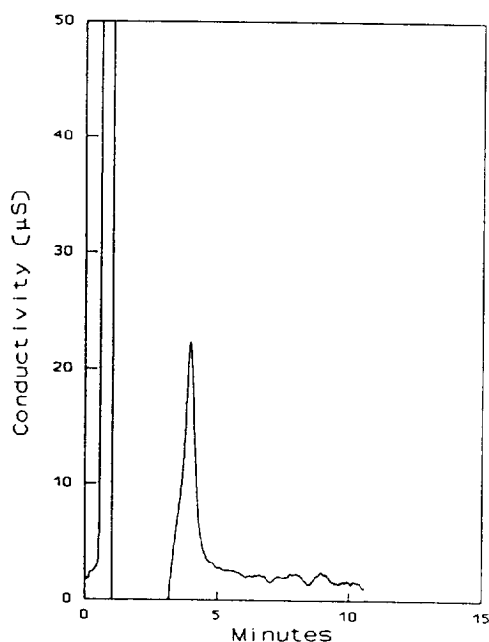


Fig. 6. Injection of 200  $\mu$ l of toluene with 50 ppb aniline and 0.75 mM methanesulfonic acid. The eluent is 0.75 mM methanesulfonic acid in methanol at 1.5 ml/min.

as the criteria, a detection limit of 5 ppb was determined. This type of trace analysis should be applicable to many bases in organic solvents.

#### 4. Conclusions

A plot of  $\log t'_R$  vs.  $\log H^+$  (from methanesulfonic acid) is linear with a slope close to  $-1$  in each of the four solvents studied. This is an indication that the separation mechanism is pure ion exchange and not partition based on hydrophobic attraction. The retention factors of  $C_1$ – $C_9$  alkylamine cations show very little change with regard to the number of carbon atoms. However, amine cations, such as aniline, N-methylaniline and N,N-dimethylaniline, are easily separated. These results indicate that the size and shape of the cation may affect the ion-exchange selectivity.

Practical separations of amine cations can be obtained in methanol or ethanol with indirect conductivity detection. Large concentrations of neutral organic compounds in the sample do not interfere with the chromatographic separation and determination of cations.

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