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Ion chromatographic separation of alkali metals in organic solvents

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Abstract

Ion-exchange chromatography is a common method for the separation and determination of metal cations. Although much research has been done on improving various aspects of this technique, the use of non-aqueous eluents has received little attention. The effect of organic solvents on the retention of alkali-metal cations on a macroporous polystyrene–divinylbenzene resin was studied. The retention of alkali cations increases as the organic content in the eluent increases for most organic solvents. Methanol was an exception with a maximum retention occurring at an eluent composition of methanol–water (75:25). Since organic solvents do not solvate these cations in the same manner as water, increases in the separation factors and changes in elution order are observed. Several separations that are not possible with aqueous eluents will be shown.

The effect of crown ethers in the mobile phase was also investigated. In most solvents 18-crown-6 (18C6) altered the retention of all cations. In some cases 18C6 changed elution order or improved peak shape. Separations with an organic eluent and 18C6 modifier will also be shown.

1. Introduction

Factors that influence the aqueous selectivity of cation-exchange resins for various 1+ metal cations have been studied extensively over many years. Diamond and co-workers [1,2] proposed a theory of water-enforced ion pairing to explain selectivity toward various cations. Electrostatic attraction of the sulfonate groups within the ion-exchange resin for alkali-metal cations suggests that cations with the smallest ionic radii would be the most strongly retained. The Pauling radii in Table 1 [3] would predict a chromatographic elution order of Cs^+ , Rb^+ , K^+ , Na^+ , Li^+ , which is exactly the opposite of that observed in ion-

exchange chromatography. However, hydrated ionic radii and approximate hydration number (Table 1) are in the opposite order to the Pauling radii, with Li^+ being the most highly hydrated. The cation-exchange resins used in classical ion-exchange chromatography are highly sulfonated and take up a great deal of water inside the microporous resin. The hydration of the alkali-metal ions thus would remain much the same inside the resin as in the aqueous mobile phase.

The effects of performing ion-exchange separations in aqueous–organic or in organic solvents have been studied by a number of investigators. A recent review concludes that ion exchange in non-aqueous solvents is very complicated from a theoretical point of view [4]. Organic solvents

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Table 1
Ionic radii of alkali metal cations

	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Pauling radii (Å)	0.60	0.96	1.33	1.48	1.69
Hydrated radii (Å)	3.40	2.76	2.32	2.28	2.28
Approximate hydration number	25.3	16.6	10.5	10.0	9.90

are obviously going to affect the solvation of alkali-metal cations compared to the situation in water alone. The dielectric constant, viscosity, and other effects will also be different in organic solvents.

In the present work the ion chromatographic separation of alkali-metal ions and the ammonium ion was studied in aqueous–organic mixtures of four different organic solvents and in the organic solvents which contain little, if any, water. Some major changes in selectivity were observed and several practical separations were obtained.

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- μ l sample which was detected with an 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, Taunton, MA, USA) with Labtech Notebook software (Laboratory Technologies, 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- μ m macroporous polystyrene–divinylbenzene (Sarasep, Santa Clara, CA, USA). A 2-g amount of resin was slurried with a few milliliters of glacial acetic acid and placed in an ice bath. A 5-ml volume of concentrated sulfuric acid was added to the resin with stirring. The resin mixture was reacted for 30 s then poured into ice water to quench the reaction. This procedure produced a sulfonic acid cation-exchange resin with a capacity of approximately 0.15 mequiv./g. Absolute ethanol was punctilious grade and used as obtained from Quantum Chemicals (Newark, NJ, USA). All other organic eluents used were of HPLC grade and used as obtained from Fisher Scientific (Pittsburgh, PA, USA) and Sigma (St. Louis, MO, USA). The salts and methanesulfonic acid eluent were all of reagent grade and used as obtained from Aldrich (Milwaukee, WI, USA) and Fisher Scientific. Either halide or acetate salts were dissolved in organic solvents to prepare 1000 ppm stock solutions which were then diluted with eluent to produce samples of desired concentrations.

3. Results and discussion

3.1. Type of resin

Ion chromatographic separations of alkali-metal cations are generally performed with sulfonated microporous polymeric resins [5,6] or with resins coated with a sulfonated latex. A

lightly sulfonated macroporous resin with a very high degree of cross-linking was selected for the present study. Such a resin would be less likely to undergo volume changes due to swelling and should be more compatible with organic solvents.

A separation of alkali-metal ions was first attempted in water alone using the lightly sulfonated macroporous cation exchanger with aqueous 3 mM methanesulfonic acid as the eluent. Under these conditions the sample cations exhibited very similar retention times (Fig. 1). A much better separation would be obtained with a microporous cation exchanger [5]. The selectivity of the macroporous resin for alkali-metal ions was improved considerably by chemically introducing hydroxymethyl groups [7] prior to sulfonation.

These results seem to indicate that solvation of the resin plays a role in imparting selectivity for the various sample ions. Microporous cation-exchange resins form a gel and are highly hydrated within. With sulfonated macroporous resins the hydrated alkali-metal ions may be repelled somewhat by the hydrophobic resin matrix. The presence of hydroxymethyl groups on

the macroporous resin makes it less hydrophobic and improves selectivity for the hydrated alkali ions.

When the macroporous resin column in Fig. 1 was used with the same acidic eluent in 100% methanol, the chromatographic separation was improved considerably (Fig. 2). Now the alkali-metal ions are solvated with methanol and the resin matrix is probably coated with a thin layer of methanol, which makes the ions and the resin surface more compatible with one another.

3.2. Ion chromatography in organic solvents

Ion-exchange selectivity in organic solvents and in mixed solvents involves a complex series of effects. The dielectric effect and ionic solvation seem to play the major roles, but interactions involving the solvent, resin exchange sites, analyte ion, and eluting ion also affect retention [8].

Capacity factors for the alkali-metal cations were measured in eluents containing 0–100% organic solvent (Table 2). The retention factors (capacity factor), k' , of the cations generally increase with greater organic content of the

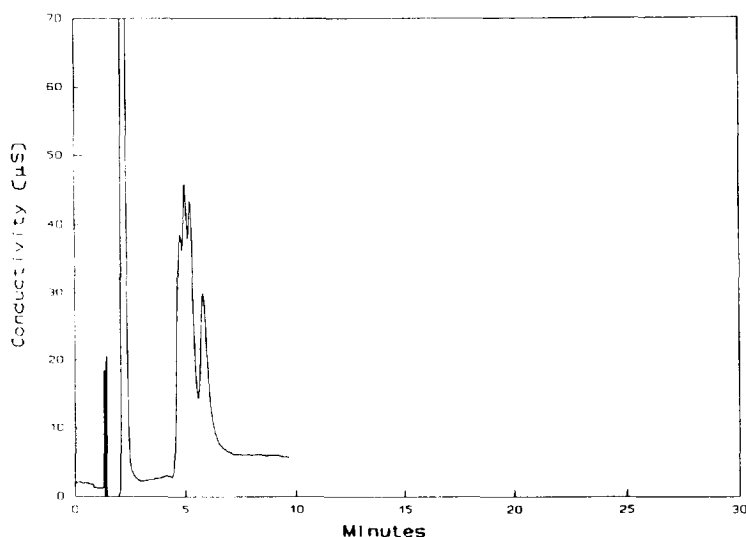


Fig 1. Separation of Li^+ (2 ppm), Na^+ (5 ppm), K^+ (16 ppm), Rb^+ (24 ppm) and Cs^+ (48 ppm) on a 15-cm cation-exchange column with 3 mM methanesulfonic acid in water as the eluent.

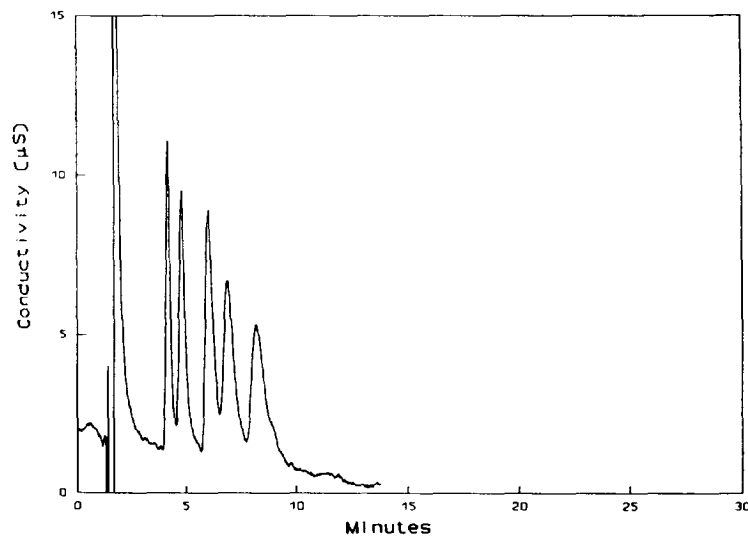


Fig. 2. Same separation as in Fig. 1 with 3 mM methanesulfonic acid in methanol as the eluent.

Table 2
Capacity factors in organic and mixed solvents with 0.5 mM methanesulfonic acid as the eluent

Solvent	k'					
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	NH ₄ ⁺
Water, 100%	2.27	2.27	2.71	2.74	2.96	3.04
<i>Methanol</i>						
25%	2.66	2.47	2.77	2.80	2.98	3.13
50%	3.10	3.07	3.31	3.39	3.80	3.70
75%	4.43	5.07	6.32	7.30	8.33	5.82
100%	2.08	2.82	3.73	4.33	5.15	3.09
<i>Ethanol</i>						
25%	2.75	2.57	2.78	2.78	2.96	3.13
50%	3.25	3.09	3.37	3.48	3.76	3.78
75%	4.61	5.14	6.90	7.62	8.76	5.98
100%	1.86	3.84	7.24	8.84	9.87	2.12
<i>2-Propanol</i>						
25%	2.20	1.98	2.11	2.05	2.17	2.45
50%	2.26	2.14	2.35	2.41	2.62	2.88
75%	3.41	3.52	4.42	4.81	5.66	4.69
100%	8.84	12.3	19.5	>20	>20	4.54
<i>Acetonitrile</i>						
25%	2.10	2.10	2.37	2.38	2.54	2.51
50%	2.50	2.38	2.89	2.98	3.35	3.10
75%	3.00	3.12	3.79	3.95	4.45	3.98
100%	4.46	2.11	1.75	1.59	1.54	2.40

solvent. This trend was observed for all eluents up to a composition of organic–water (75:25). Retention decreased when the organic content was increased to 100% for all cations in methanol and several cations in acetonitrile and ethanol. Increased retention of sample cations may be explained at least partly by the lower dielectric of organic solvents. This favors ion-pair formation with the result that analyte cations will be electrostatically attracted more strongly to the resin sulfonate anion. Solvation also appears to be a major force. As the organic content is increased toward 100%, analyte cations must become less solvated by water and more solvated by the organic solvent molecules which are all larger than water molecules [8]. The larger radii should inhibit the approach of the cation to the resin and therefore cause a decrease the retention times. At about 75% methanol this effect becomes more important than the continued decrease in dielectric. The data for ethanol also support this. Maxima are observed for Li^+ and Na^+ which are the most highly solvated ions. Replacing water with ethanol in the hydration sphere should have a larger effect on the solvated radii of these ions than the other less solvated alkali ions. The change in solvated radii is therefore more important for Li^+ and Na^+

than the decrease in dielectric. No maxima is observed for 2-propanol, indicating that the decrease in dielectric is more important than the change in solvation radii. The maxima in methanol are represented graphically in Fig. 3. A similar maximum has been observed by others [9–12].

Linear plots were obtained in 100% methanol for $\log k'$ vs. $\log H^+$ (methanesulfonic acid), as shown in Fig. 4. Slopes of all the cations were very close to the theoretical slope of -1.0 (± 0.02).

The separation factor for potassium/ammonium on most chromatographic systems is usually fairly small. However, the ratio of retention times is quite large in 100% ethanol: $t(\text{K}^+)/t(\text{NH}_4^+) = 7.24/2.12 = 3.4$. The chromatogram in Fig. 5 shows that an ammonium peak of only 10 ppm can easily be separated from a 1000 ppm K^+ peak. An even larger ratio of $t(\text{K}^+)/t(\text{NH}_4^+)$ is found in 2-propanol. However, the peaks in 2-propanol were much broader than in methanol and ethanol, and the sensitivity of the conductivity detector was appreciably lower.

Retention in acetonitrile followed the same general trend as with the alcohol eluents. In 100% acetonitrile a unique elution order was observed; Cs^+ eluted first and Li^+ eluted last.

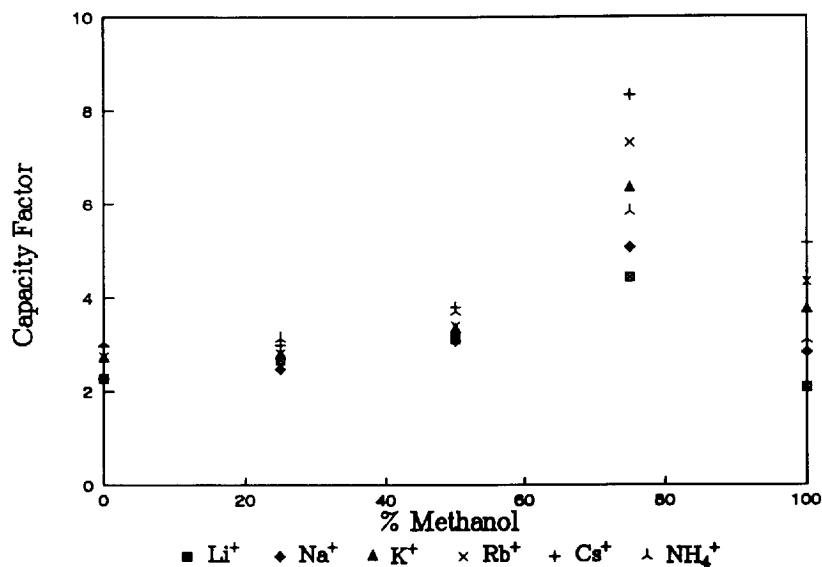


Fig. 3. Effect of methanol on the retention of alkali-metal ions. The eluent contains 0.5 mM methanesulfonic acid.

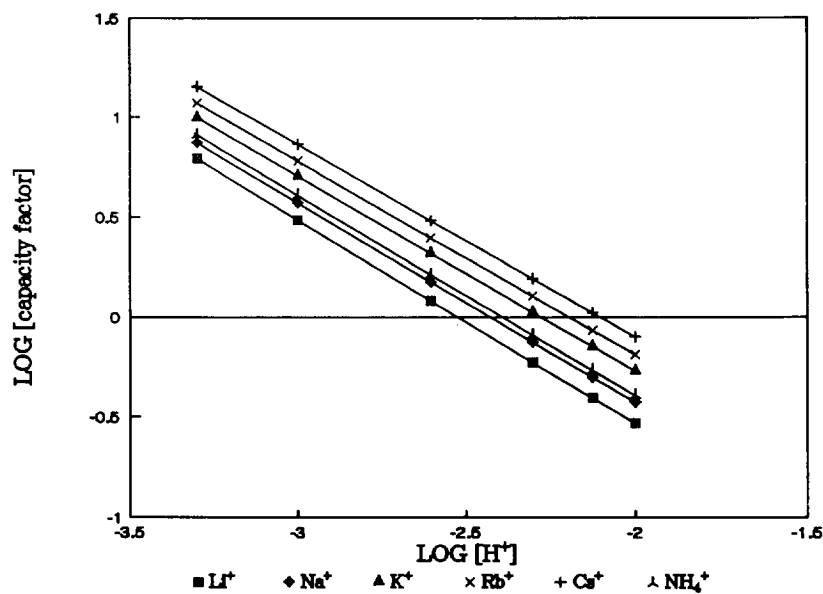


Fig. 4. Effect of methanesulfonic acid concentration on retention of alkali metals in 100% methanol.

This is the reverse of the normal elution order for the alkali metals. Unfortunately, the chromatographic peaks obtained in 100% acetonitrile were generally quite broad.

3.3. Effect of 18-crown-6

Crown ethers have been known for many years to complex alkali-metal cations [13]. In

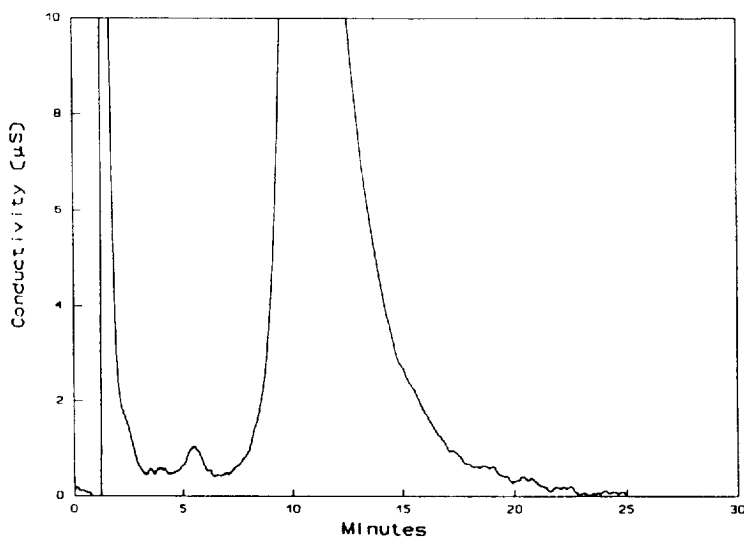


Fig. 5. Separation of 1000 ppm K^+ and 10 ppm NH_4^+ on a 10-cm column with 1 mM methanesulfonic acid in 100% ethanol as the eluent.

recent years they have been used to manipulate selectivity in ion-exchange chromatography [14–16]. Often they are used in a water–organic mobile phase to dynamically coat a silica C₁₈ or polymeric resin column. The retention mechanism involves ligand exchange rather than ion exchange.

In this research a crown ether was added the methanesulfonic acid eluent in an organic solvent. The crown ether was sufficiently soluble that no dynamic coating of the stationary phase took place [14]. This was verified by plotting $\log k'$ vs. $\log H^+$ for Li⁺ and K⁺ in organic eluents containing 10 mM 18-crown-6 (18C6); 100% acetonitrile and 75% methanol were tested. In both eluents, slopes of the Li⁺ and K⁺ lines were very close to -1.0 . If 18C6 were coating the resin, a second retention mechanism of ligand exchange would affect the K⁺ ion significantly more than the Li⁺ ion and a difference in slopes would be expected. Since the slopes were nearly identical in both eluent it was concluded that no coating was taking place and the retention mechanism was purely ion exchange.

The alkali-metal ions have larger formation constants with 18C6 in organic solvents than in water [17]. It was expected that 18C6 would increase retention due to formation of a larger cationic complex. This was found to be generally true but not necessarily because of the formation of larger cations.

The effect of 18C6 on the ion-exchange behavior of alkali metals in non-aqueous solvents is shown in Table 3. Although increasing concentrations of 18C6 in acetonitrile increase the retention factors of all of the ions studied, the large increase in the k' of lithium was the most striking. The separation factor [$k'(Li^+)/k'(Na^+)$] was 3.8 compared with 2.6 with no crown ether. The presence of the crown ether also sharpens the chromatographic peaks. This effect permitted the separation of 1 ppm Li⁺ from 500 ppm Na⁺ (Fig. 6). Data in Table 3 suggests small amounts of Li⁺ can be separated from much larger amounts of all other alkali-metal ions as well.

H⁺ does not complex 18C6 in water or metha-

Table 3
Effect of 18C6 on k' of alkali metal ions in organic solvents

	mM 18C6			
	0	0.1	1.0	10
<i>10-cm column with 2 mM methanesulfonic acid in methanol as the eluent</i>				
Li ⁺	1.45	1.31	1.32	1.34
Na ⁺	1.80	2.06	2.21	2.20
K ⁺	2.55	2.67	2.63	2.59
Rb ⁺	3.05	4.08	4.05	4.01
Cs ⁺	3.77	4.17	4.21	4.23
NH ₄ ⁺	1.93	2.71	3.34	3.36
<i>10-cm column with 1 mM methanesulfonic acid in acetonitrile as the eluent</i>				
Li ⁺	3.57	4.59	7.17	8.97
Na ⁺	1.39	1.33	1.64	2.34
K ⁺	1.34	1.26	1.65	2.48
Rb ⁺	1.26	1.26	1.73	2.45
Cs ⁺	1.24	1.27	1.71	2.74
NH ₄ ⁺	1.50	1.39	2.18	3.35

nol, but it does have a large formation constant in acetonitrile ($K_f = 10^{6.5}$) [17]. The longer retention times in acetonitrile may be a consequence of the strong complex between H⁺ and the crown ether. This complex is stronger than the 18C6 complexes with any of the alkali-metal ions. A large H⁺ complex would be a weaker eluting species than H⁺ alone and the retention times of the alkali metals would increase. The alkali-metal formation constants with 18C6 are generally higher in methanol than in acetonitrile except for Li⁺, which is not complexed. Addition of 0.1 mM 18C6 increases k' , but increasing the concentration further has little effect. H⁺ is scarcely complexed in methanol, so the changes in retention are due to the interaction of the crown ether with the metal cations. It is unclear why K⁺ is affected so little since it has the largest K_f with 18C6. The other cations generally elute in order of decreasing K_f . The metals with higher K_f values spend more time as a larger, complexed ion. The larger ions have the largest k' values in methanol.

Including NH₄⁺ in a separation with the alkali

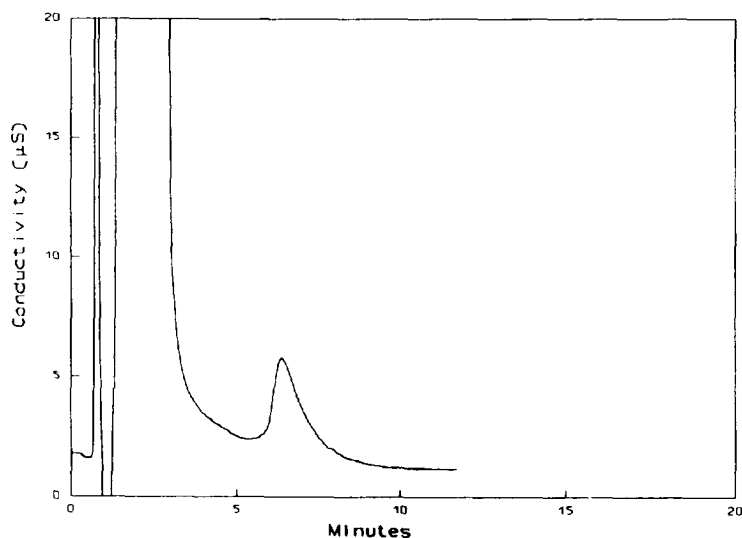


Fig. 6. Separation of 500 ppm Na^+ and 1 ppm Li^+ on a 10-cm column with 1 mM methanesulfonic acid and 1 mM 18C6 in 100% acetonitrile as the eluent.

metals was not possible in 100% methanol. It eluted very closely to Na^+ and could not be separated. The addition of 18C6 did adjust the retention times but not in a manner to allow a separation. An eluent of 75% methanol was

found to increase separation factors of several cations. Adding 18C6 to this eluent further increased the resolution and improved peak shapes. A separation of four ions in 75% methanol, 1.5 mM methanesulfonic acid and 1 mM

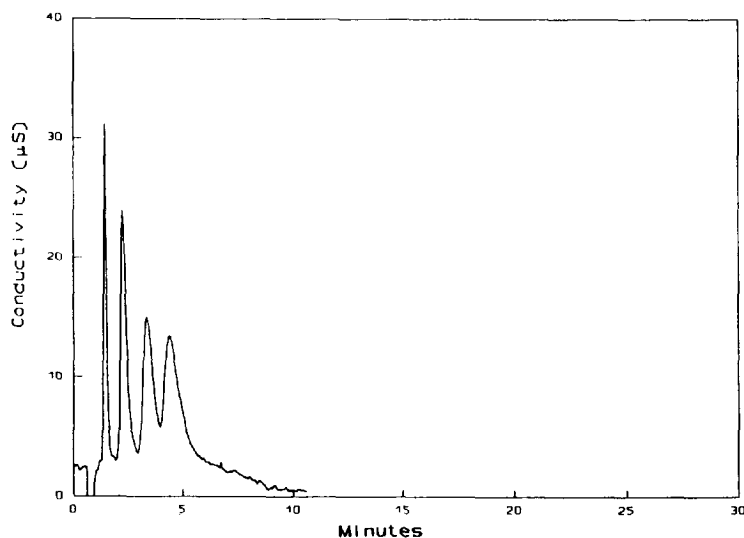


Fig. 7. Separation of Li^+ (1 ppm), Na^+ (3 ppm), NH_4^+ (3 ppm) and K^+ (9 ppm) on a 5-cm column with 1.5 mM methanesulfonic acid and 1 mM 18C6 in a 75% methanol as the eluent.

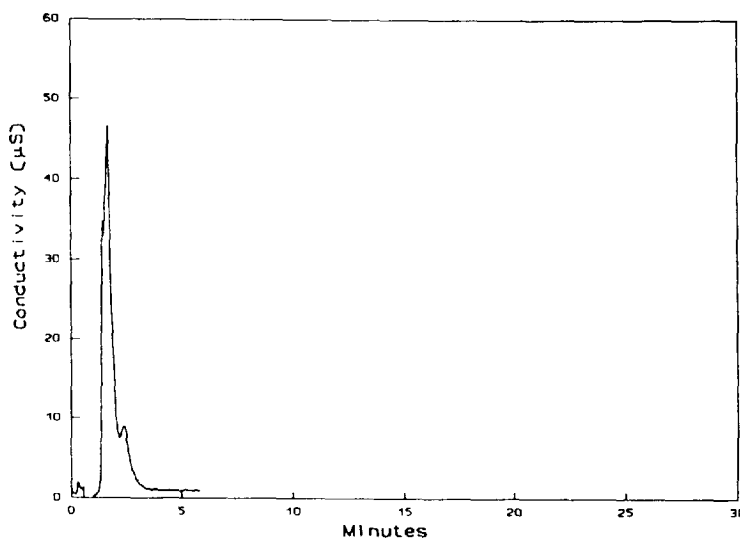


Fig. 8. Same separation as in Fig. 7 but without 18C6.

18C6 is shown in Fig. 7. The effect of 18C6 is easily seen when comparing this to a similar separation without 18C6 (Fig. 8).

4. Conclusions

The use of non-aqueous solvents with macroporous cation-exchange resin permit several separations that are very difficult with aqueous eluents. Methanol was found to be the most favorable solvent due to the best combination of resolution and peak shape. Acetonitrile and ethanol, although producing broader peaks, are useful for separating ions that usually elute close together, Li^+/Na^+ and K^+/NH_4^+ respectively. Elution order in acetonitrile is reversed from that found with aqueous eluents: $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$. Addition of 18C6 to the mobile phase improves both peak shape the resolution of several ions.

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