SUBSTITUTION-INERT METAL COMPLEX MOBILE PHASES IN NON-SUPPRESSED ANION CHROMATOGRAPHY

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SUMMARY

Substitution-inert metal complexes, sodium ethylenediaminetetraacetatocobaltate(III), Na[Co(edta)], and tris(ethylenediamine)cobalt(III) iodide, [(Co(en)$_3$]I$_3$, are used as eluting species in non-suppressed anion chromatography. Na[Co(edta)] is found to be an effective eluent species in the separation of singly charged anions whereas [Co(en)$_3$]I$_3$ is found to be a poor eluent species. Na[Co(edta)] at a concentration of $2.00 \cdot 10^{-3}$ M is able to completely separate nitrite, bromide, and nitrate ions in approximately 21 min on a Vydac 302IC4.6 anion-exchange column. Fluoride and chloride ions co-elute. Bicarbonate, dihydrogen phosphate, perchlorate, iodide, and sulfate ions are not detected by this system. The non-optimized detection limits for the detectable anions range from 5–25 ppm for an injection of 20 μl sample. Using the same column, [Co)en)$_3$]I$_3$ at a concentration of $5.53 \cdot 10^{-5}$ M is able to separate chloride, nitrite, and bromide ions in approximately 80 min. Nitrate and sulfate ions are not detected. Other ions were not tested. Under conditions of these experiments, Vydac 302IC4.6 anion-exchange columns have a limited lifetime of less than ten weeks. Columns from the same batch are shown to produce different results.

INTRODUCTION

The separation and determination of ions using ion chromatography has been a versatile technique, particularly for anions. Two types of instrumental design are known. The current suppressed ion chromatography used a hollow fiber ion-exchange membrane with a gravity feed flow of sulfuric acid to reduce the background signal after ion-exchange separation has occurred[1-3]. This method usually gives lower detection limits for various anions but the choice of eluent is limited to the amenability to suppression by the suppressor. On the other hand, the non-suppressed ion chromatography normally applies a low capacity column and a conductivity meter capable of electronically suppressing the background signal[4]. The design is slightly simpler and a variety of eluents can be used. However, it does suffer from higher detection limits occasionally.

Because of the availability of conventional high-performance liquid chromatographic instrumentation, non-suppressed ion chromatography can be easily practiced

in most analytical laboratories. For the separation of anions, aromatic acid solutions such as phthalic acid and benzoic acid buffered at pH 5 to 6 have been used most often as eluents due to their intrinsic low specific conductances. It is also found that the resin capacity and eluent concentration can be varied in tandem to increase the sensitivity of anion chromatography. On the other hand, the selectivity of ion chromatography seems to be limited by the resin phase due to hydrophobic absorption and the nature of the ion-exchange functional groups if ion-exclusion mechanism is not considered[5].

We have been interested in applying substitution-inert transition metal complexes in liquid chromatographic separations. Previously, we have demonstrated that when cobalt(III) complexes are covalently bonded to silica support, unique selectivities can be achieved[6]. In the field of ion chromatography, it is possible to use these metal complex solutions as eluents because they normally have low specific conductances. This is also promised by the work of Inczedy and co-workers for the separation of oxalate ion and sulfate ion[7] as well as the resolution of aspartic acid and mandelic acid[8] using such species as eluents.

This paper reports the effects of sodium ethylenediamintetraacetato-cobaltate(III), Na[Co(edta)], and tris(ethylenediamine)cobalt(III) iodide, [Co(en)$_3$]I$_3$, in the mobile phase on the separation of a number of inorganic anions. These complexes are chosen because they are easily synthesized and well-characterized. Furthermore, they are substitution-inert metal complexes. As such, they will not readily undergo ligand exchange during the relatively short chromatographic process. This characteristic insures that the interactions between the anions under investigation and the metal complex will be due solely to outer-sphere ion interactions.

EXPERIMENTAL

Reagents and solutions

Na[Co(edta)] was prepared by the method outlined by F. P. Dwyer *et al.*[9]. The crystals were recrystallized twice and dried for 24 h at 50°C. Reagent grade phthalic acid and sodium salts of all anions investigated were dried for 24 h at 110°C.

Eluent and 100-ppm sample solutions were prepared by diluting appropriate amounts of reagent in boiled deionized water or 18 MΩ reagent grade water. Sample solutions of smaller concentrations were prepared by successive dilution.

The pH of the $2.00 \cdot 10^{-3}$ M phthalic acid solution was adjusted to 5.0 with sodium borate; pH adjustments were not made on any other solution.

Instrumentation

The experiments were conducted using the following apparatus: (1) a Waters Model 6000A solvent delivery system, (2) a Rheodyne injector fitted with a 20-μl sample injection loop, (3) a Vydac 302IC4.6 anion chromatography column, (4) a Perkin-Elmer LC-21 conductivity detector and (5) a linear strip-chart recorder.

A Milli-Q Type I regent grade water system was used to obtain 18 MΩ water for eluent preparation. A Kernco Model 671 pH meter fitted with an Orion combination pH electrode was used to measure the pH of solutions and a Mettler type H6 analytical balance was used to weigh regents.

Procedure

Every time a new eluent species was introduced, the column was conditioned with 1 l of that eluent. Prior to injections, the column was permitted to equilibrate until a steady baseline was observed. Samples (25 μl) were injected periodically with a Hamilton No. 702 syringe. Mixtures as well as single anion samples were injected. Identification of peaks in the mixture were made by correlating single ion sample retention times with retention times of the components of the mixture. A minimum of three determinations was made for each sample. The flow-rate was maintained at 2.0 ml/min. The temperature of the column was not controlled. Room temperature varied between 21 and 24°C.

In order to examine whether ion-pairing occurred during the separation, [Co(en)$_3$]I$_3$ solutions were also used as eluent. The chromatographic procedures were the same as those for Na[Co(edta)] eluent.

RESULTS AND DISCUSSION

Vydac 302IC4.6 anion-exchange columns have a limited lifetime. This is evidenced by Figs. 1 and 2. Fig. 1, one of the first chromatograms obtained of a mixture of a number of ions shows quick and complete separation. Fig. 2, a chromatogram produced after ten weeks of use shows incomplete separation. Nitrite and bromide ions are co-eluting.

Two Vydac columns (serial numbers 70 and 71) used in this experiment are from the same batch and yet produce different results. The initial chromatograms obtained from each column use phthalic acid as the eluent species. Under the same conditions, the retention times of the ions were longer for No. 70 than for No. 71 (Table I). This suggests that the capacity of column No. 70 is greater than the capacity of column No. 71. However, the retention times for the ions separated with Na[Co(edta)] eluent were longer for column No. 71 even though a higher concentration of the eluent species is used (Table II). This results because the data from column No. 70 was obtained after it had begun to degrade. The degradation of a column results in fewer available active sites which means there is a decrease in column capacity. Therefore, under the same conditions, the retention time for ions chromatographed on such a column would be less than those on a similar, but new, column.

Gjerde *et al.*[10] have derived an equation to account for the effect of eluent concentration on the retention time:

$$\log t' = -\frac{y}{x} \log [\text{eluent}] - \text{constant} \tag{1}$$

where t' is the adjusted retention time, y and x are the charges of the sample anion and eluent anion, respectively. As eqn. 1 suggests, there is a linear relationship between $\log t'$ and $\log$ [eluent]. A plot of five ions detected by the Na[Co(edta)] system is shown in Fig. 3. The slopes for these ions are very similar ranging from 0.72 to 0.76. The correlation coefficient for each line is greater than 0.99. The problem of the deviation of the slopes from the theoretical expectations, *i.e.* one, can not be resolved at the moment. However, it was also observed in other studies[10]. On the
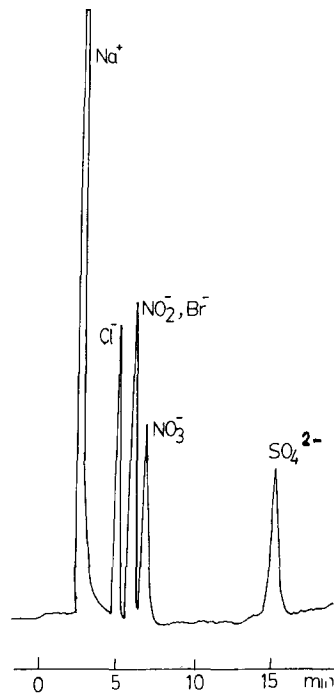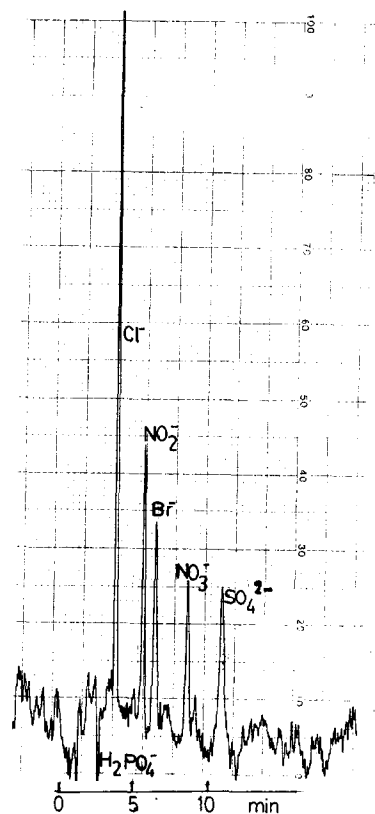
Fig. 1. Chromatogram of anions on a fresh Vydac column. Eluent, $2.00 \cdot 10^{-3}$ M phthalic acid (pH = 5.0); sample, 25 ppm mixture of NaCl, NaNO$_2$, NaF, NaBr, NaNO$_3$, NaH$_2$PO$_4$, NaI, NaHCO$_3$, NaClO$_4$ and Na$_2$SO$_4$ (25 μl injection); flow-rate, 2 ml/min. Initial chromatogram obtained from column No. 71.

Fig. 2. Chromatogram of anions on a dedrading Vydac column. Conditions are the same as Fig. 1 except sample concentration is a mixture of NaCl, NaNO$_2$, NaBr, NaNO$_3$ and Na$_2$SO$_4$, each is 100 ppm. Chromatogram was obtained from column No. 70 after ten weeks of use.

TABLE I

RETENTION TIMES (min) OF FIVE ANIONS ILLUSTRATING DIFFERENCES IN BATCH-MATE VYDAC 302IC4.6 COLUMNS

Eluent, $2.00 \cdot 10^{-3}$ M phthalic acid (pH = 5.0); flow-rate, 2 ml/min. Data from initial chromatograms for each column.

Ion	Column No. 70	Column No. 71	t_{70}/t_{71}
Cl$^-$	3.3	2.4	1.4
NO$_2^-$	5.4	4.2	1.3
Br$^-$	6.5	5.0	1.3
NO$_3^-$	9.0	7.2	1.3
SO$_4^{2-}$	15.3	9.4	1.6

TABLE II

RETENTION TIMES (min) OF FIVE ANIONS ILLUSTRATING DIFFERENCES IN BATCH-MATE VYDAC COLUMNS

Eluent, $4.00 \cdot 10^{-4}$ M Na[Co(edta)] for column No. 70 and $5.00 \cdot 10^{-4}$ M Na[Co(edta)] for column No. 71; flow-rate, 2 ml/min. Column No. 70 data are from an aging column. Column No. 71 data are from a new column. ND = Not detected.

Ion	Column No. 70	Column No. 71	t_{70}/t_{71}
Cl^-	18.6	32.4	0.57
NO_2^-	21.8	43.6	0.50
Br^-	23.2	52.2	0.44
NO_3^-	25.7	64.4	0.40
SO_4^{2-}	ND	ND	
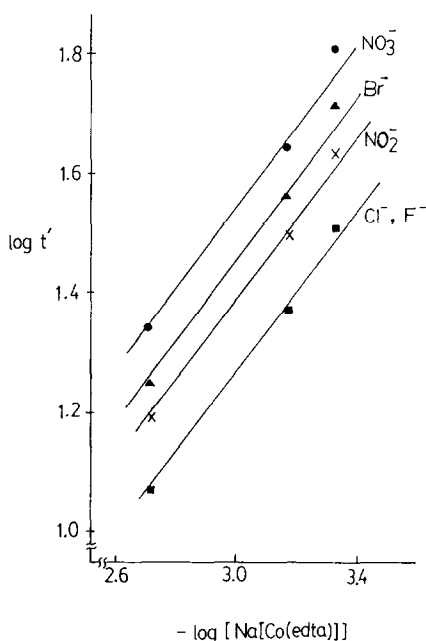
Fig. 3. Plot of log t' vs. $-\log$ {Na[Co(edta)]} for five anions.

other hand, the similar values of slope for various anions indicate that change of eluent concentration may only alter the retention time of each sample anion but not the elution order of two peaks.

Retention times (Table III) are much shorter for the phthalic acid system than for the metal complex systems. A phthalic acid eluent at $2.00 \cdot 10^{-3}$ M and pH = 5.0 separates a mixture of ions in approximately 7 min. A Na[Co(edta)] eluent at the same concentration requires 22 min to effect a similar separation. This suggests that phthalic acid competes more strongly for the active column sites than does Na[Co(edta)]. In addition, at pH = 5.0 the phthalic acid solution is composed of

TABLE III

COMPARISONS OF RETENTION TIMES (min) OF VARIOUS ANIONS WITH THREE ELUENTS (VYDAC 302IC4.6 COLUMN)

ND = not detected, − = not injected.

Ion	Phthalic acid, $2.00 \cdot 10^{-3}$ M, $pH = 5.0$	Na[Co(edta)], $2.00 \cdot 10^{-3}$ M, $pH = 5.3^\star$	[Co(en)$_3$]I$_3$, $5.53 \cdot 10^{-5}$ M, $pH = 5.6^\star$
$H_2PO_4^-$	1.5	ND	−
F^-	2.5	11.6	−
Cl^-	2.4	11.8	55.2
NO_2^-	4.2	15.6	72.2
Br^-	5.0	17.8	80.4
NO_3^-	7.2	21.9	ND
SO_4^{2-}	9.4	ND	ND
HCO_3^-	ND	ND	−
ClO_4^-	ND	ND	−
I^-	ND	ND	−

* Natural pH.

72% of the singly charged species and 28% of the doubly charged species. A doubly charged species will be more strongly retained by the stationary phase than a single charged species[11].

The retention time for elution by [Co(en)$_3$]I$_3$ at a concentration of $5.53 \cdot 10^{-5}$ M is unacceptably long. Iodide is known to be a poor eluting ion because its ΔH of hydration is lower and its polarizability greater than the inorganic ions chromatographed[11]. Its concentration was also much lower than the phthalic acid eluent. Therefore, this should be expected.

As Table III indicates, the metal complex systems were unable to detect sulfate ion whereas phthalic acid did so. This can be attributed to phthalic acid's ability to compete effectively with SO_4^{2-} for exchange sites because of the presence of the divalent phthalate ion.

F^- and Cl^- co-eluted in both systems. $H_2PO_4^-$ was detected by the phthalic acid system but not by the Na[Co(edta)] system. HCO_3^- and ClO_4^- were not detected by either system presumably due to comparable conductivity with the eluent. I^- was strongly adsorbed in the resin phase and did not elute.

No changes in anion elution order occurred. This is expected because the separation mechanism is dependent only on the differences in attraction of the sample ions and the eluent ion for packing sites. The sample ions retain their electrostatic characteristics; *i.e.* NO_2^- associates more strongly with the packing than does Cl^-.

The approximate detection limits of commonly detected anions in the phthalic acid system and in two different eluent concentrations of Na[Co(edta)] are listed on Table IV. Fluoride, chloride, and nitrite ions have the same detection limits in the three systems. Bromide and nitrate ions are detected to a comparable degree in these systems with phthalic acid being the most sensitive, Na[Co(edta)] at $7 \cdot 10^{-4}$ M, the intermediate, and Na[Co(edta)] at $2 \cdot 10^{-3}$ M being the least sensitive. Na[Co(edta)] is probably slightly less effective because of increased retention time. Increased re-

TABLE IV

COMPARISONS OF DETECTION LIMITS (ppm) OF VARIOUS ANIONS FOR THREE ELUENTS
(VYDAC 302IC4.6 COLUMN)

Sample injection, 20 μl. ND = Not detected.

Ion	Phthalic acid, 2.00 · 10^{-3} M, pH = 5.0	Na[Co(edta)], 2.00 · 10^{-3} M, pH = 5.3*	Na[Co(edta)], 7.00 · 10^{-4} M, pH = 5.4*
$H_2PO_4^-$	25	ND	ND
F^-	5	5	5
Cl^-	5	5	5
NO_2^-	10	10	10
Br^-	10	25	10
NO_3^-	10	25	25
SO_4^{2-}	25	ND	ND
HCO_3^-	ND	ND	ND
ClO_4^-	ND	ND	ND
I^-	ND	ND	ND

* Natural pH.

tention time results in band broadening which can in turn cause the peak height to shrink. Na[Co(edta)] is probably slightly less effective because of increased retention time. Increased retention time results in band broadening which can in turn cause the peak height to shrink. The lower concentration of Na[Co(edta)] produces slightly better detection than the higher concentration because its background noise is much lower. This is a direct result of the concentration difference; the lower the concentration the lower the conductivity[12]. The detection limits for ions using [Co(en)$_3$]I$_3$ as the eluent were not determined. With 150 ppm salt solutions, the peaks were barely detectable. Better detection limits can be expected when these systems are optimized.

Peak integrity can be ascertained by a comparison of Figs. 1, 4 and 5. One notes that the peaks using phthalic acid and Na[Co(edta)] solutions as eluents are sharp and Gaussian in shape. This is indicative of effective mobile and stationary phase interaction. On the other hand, peaks using [Co(en)$_3$]I$_3$ eluent have an odd shape. The ions seem to have been pushed out of the column. This may be indicative of sample ions being desorbed by the strongly adsorbed iodide ion and their pairing with the [Co(en)$_3$]$^{3+}$ ion. It is known that this phenomenon is not occurring with the Na^+ ion in the Na[Co(edta)] system from work done by Jenke and Pagenkopf[13]. However, in the case of [Co(en)$_3$]$^{3+}$, ion-pairing cannot be excluded and may account for the curious peak shape.

One may also note that the phthalic acid systems shows a negative peak for $H_2PO_4^-$. This indicates that the conductivity of $H_2PO_4^-$ is less than that of the eluent[13].

The resolution of the peaks can best be described by α, the selectivity factor (Table V).
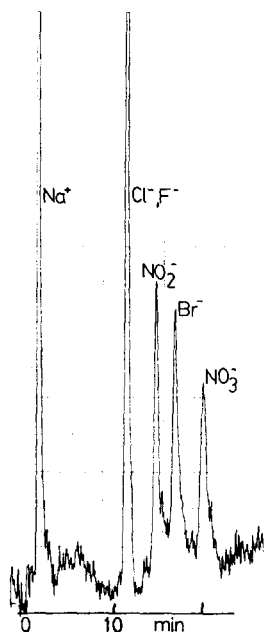
$$\alpha = (t_a - t_0)/(t_b - t_0) \qquad (2)$$

Fig. 4. Chromatogram of anions separated by a mobile phase of $2 \cdot 10^{-3}$ M Na[Co(edta)], pH = 5.3. Sample, 50 ppm mixture of sodium salts of Cl^-, F^-, NO_2^-, Br^-, NO_3^-, HCO_3^-, I^-, $H_2PO_4^-$, ClO_4^- and SO_4^{2-}; flow-rate, 2 ml/min.
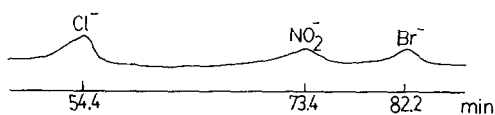

Fig. 5. Chromatogram of anions separated by a mobile phase of $5.53 \cdot 10^{-5}$ M [Co(en)$_3$]I$_3$. pH = 5.6. Sample, 150 ppm mixture of sodium salts of Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-}; flow-rate, 2 ml/min.

TABLE V

COMPARISONS OF SELECTIVITY FACTORS FOR ANION SEPARATIONS WITH THREE ELUENTS (VYDAC 302IC4.6 COLUMN)

ND = Not detected, — = not injected.

Ion	Phthalic acid, $2.00 \cdot 10^{-3}$ M, pH = 5.0	Na[Co(edta)], $2.00 \cdot 10^{-3}$ M, pH = 5.3*	[Co(en)$_3$]I$_3$, $5.53 \cdot 10^{-5}$ M, pH = 5.6*
SO_4^{2-}	1.3	ND	—
HCO_3^-	1.4	1.2	—
Br^-	1.2	1.1	1.1
NO_2^-	1.8	1.3	1.3
Cl^-	0.96	1.0	—
F^-	1.7	ND	—
$H_2PO_4^-$			

* Natural pH.

t_a and t_b are retention times of ions a and b, respectively, t_0 is the retention time of the solvent peak. If α is approximately equal to 1 then sample a and b co-elute. If α is greater than 1.1 then the samples are well separated.

Fluoride and chloride ions co-elute in the phthalic acid and Na[Co(edta)] systems. All other detected ions are well separated. A comparison to the phthalic acid and complex systems show that the selectivity factors are greater for the phthalic acid than for the complexes. This indicates that the phthalic acid separates peaks to a greater extent than the complexes. In a sense, the peaks are further apart.

CONCLUSIONS

It has been observed that Vydac columns have a limited lifetime. It has been shown that Na[Co(edta)] can act as an effective eluent in the separation of singly charged anions in non-suppressed anion chromatography. Its advantage is that it requires no pH adjustment as does phthalic acid. However, it takes longer to effect separation. In addition, the retention order of the anions is the same regardless of the eluent. [Co(en)$_3$]I$_3$ was shown to be ineffective in anion-exchange chromatography. However, it may prove to be an excellent eluent in cation chromatography.

ACKNOWLEDGEMENTS

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