Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Application of the Bifunctional Switch-Type Cryptand Ion Chromatographic Stationary Phase for Ion Separation

Su-Shing Tsai; Jeng-Shong Shih

To cite this Article Tsai, Su-Shing and Shih, Jeng-Shong(1998) 'Application of the Bifunctional Switch-Type Cryptand Ion Chromatographic Stationary Phase for Ion Separation', Separation Science and Technology, 33: 10, 1407 — 1421
To link to this Article: DOI: 10.1080/01496399808545057
URL: http://dx.doi.org/10.1080/01496399808545057

SEPARATION SCIENCE AND TECHNOLOGY, 33(10), pp. 1407–1421, 1998

Application of the Bifunctional Switch-Type Cryptand Ion Chromatographic Stationary Phase for Ion Separation

SU-SHING TSAI and JENG-SHONG SHIH*
DEPARTMENT OF CHEMISTRY
NATIONAL TAIWAN NORMAL UNIVERSITY
TAIPEI, TAIWAN 11718, REPUBLIC OF CHINA

ABSTRACT

Poly(styrene/divinylbenzene) resin with cryptand 22 as an anchoring group was synthesized and applied in ion chromatography as a packing material for separations of organic anions as well as cations. The cryptand can not only form strong complexes with metal cations, but it has also shown a remarkable complexing ability with organic anions after protonation at pH < 7. The protonated cryptand resin has been applied as an anion exchanger to successfully separate some organic carboxylate anions including $HCOO^-$, CH_3COO^-, $CH_3CH_2COO^-$, and $CH_3(CH_2)_2COO^-$, and some geometric isomers, e.g., fumarate and maleate ions, with water as the eluent. Alternatively, after deprotonated at pH > 7, the cryptand resin can be switched as a cation exchanger to separate inorganic cations. The effects of solvents, temperature, pH values, and flow rates of eluents on the separation of organic anions were also investigated.

Key Words. Cryptand; Ion chromatography; Separation of organic anions

INTRODUCTION

Artificial macrocyclic polyethers such as crown ethers and cryptands have demonstrated a remarkable ability to complex various metal ions (1–6), and

* To whom correspondence should be addressed.

their applications in the separation and analysis of metal ions have been extensively studied (7–11). Owing to their high selectivity in forming complexes with metal ions, crown ethers and cryptands are expected to be suitable column materials in ion chromatography for the separation of metal ions. However, there is no information available on the use of macrocyclic polyether packing material for the separation of organic anions. This is largely due to a preference for the use of crown ethers as packing materials and the inability of crown ethers to form complexes with anions. It is well known that cryptands not only can form complexes with metal ions like crown ethers, but also can form complexes with anions after protonation in acidic solutions (12–16). Therefore, in this study a so-called "switch-type" cryptand ion chromatographic stationary phase was prepared for separations of metal ions as well as organic anions. Cryptand stationary phases can serve as cation exchangers at pH $\geqq$ 7 for the separation of cations, and they can be switched into anion exchangers after protonation at pH $<$ 7 for the separation of organic anions. In this work, XAD-4 (poly(styrene/divinylbenzene)) resin with cryptand-22 as an anchoring group was prepared and applied as a bifunctional switch-type ion chromatographic packing material for the separations of organic anions such as carboxylate anions and metal ions, e.g., alkali, alkali earth, and some transition metal ions. A systematic investigation of the separation of organic anions, including the effects of solvents, temperature, pH, and flow rates of eluents, was also made and is discussed.

EXPERIMENTAL

Preparation of Cryptand Stationary Phase

The overall preparation of the cryptand stationary phase, poly(styrene/divinylbenzene)-cryptand-22, is depicted in Fig. 1. The details of this procedure were described in a previous report (16). Poly(styrene/divinylbenzene) resin (200–400 mesh) XAD-4 was used as a starting material to synthesize chloromethylated-XAD resin (XAD-CH_2Cl) with $AlCl_3$ and chloromethyl ether as shown in Fig. 1. An acidic resin (XAD-CH_2COOH) was obtained after substitution of Cl and CN with KCN and acidification with H_2SO_4. The acidic resin was chlorinated with thionyl chloride, and the acylchloride (XAD-CH_2COCl) resin was obtained. Finally, the poly(styrene/divinylbenzene)-cryptand (XAD-CH_2CO-cryptand-22) resin was synthesized by the reaction of acylchloride resin and cryptand-22. The cryptand resin was identified by infrared spectrophotometry with absorption peaks at 1638 and 1238 cm^{-1} due to the N—H and C—N stretching vibrations, respectively.

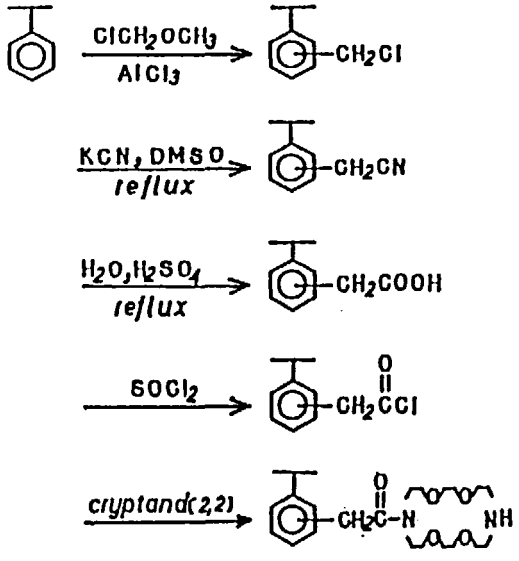


FIG. 1 Scheme for the synthesis of the cryptand resin.

Evaluation of Resin Capacity and Column Performance

The maximum adsorption capacity of the cryptand resin was calculated in terms of the number of mmoles of cryptand-22 per gram of resin following an elemental analysis of the resin. The exchange capacity of the cryptand resin was also estimated in terms of adsorption (in meq) of *cis*-butenedioate anion (maleate anion) in 1 gram of resin and was determined spectrophotometrically at 210 nm where the *cis*-butenedioate anion showed absorption.

The theoretical number of plates (N) and the height equivalent to theoretical plate (HETP) of the cryptand column were calculated according to the following equations (17, 18):

$$N = 5.54(t_r/\omega_{1/2})^2 \quad (1)$$

and

$$\text{HETP} = L/N \quad (2)$$

in which t_r and $\omega_{1/2}$ are the retention time and peak width at half the peak height of each peak, respectively, and L is the column length. The resolution (R) between the two peaks a and b was estimated with the following equation (19):

$$R = 2[(t_r)_b - (t_r)_a]/(\omega_b + \omega_a) \quad (3)$$

where $(t_r)_b$, $(t_r)_a$ and ω_b, ω_a are retention times and peak widths of the two peaks *a* and *b*, respectively.

Apparatus

A Dionex IC-4000i Ion Chromatograph with a 30 × 0.4 cm-i.d. poly(styrene/divinylbenzene)-cryptand resin column and a conductivity detector was used to separate and detect carboxylic anions and metal ions with an injection volume of 10 μL. The cryptand column was prepared at 3000 psi with a packer (JASCO SC-30) connected to a pump of a High Performance Liquid Chromatograph (JASCO BIP-B1). A Perkin-Elmer IR-983 Infrared Spectrophotometer was used to identify the components of the synthesized cryptand resin and its intermediates, and a Perkin-Elmer 240C Elemental Analyzer was employed for elemental analysis of the cryptand resin.

Chemicals

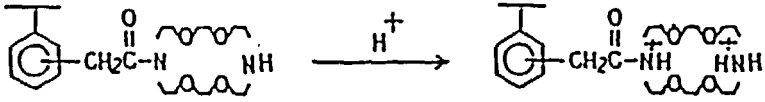
Cryptand-22 was obtained from E. Merck (Darmstadt, Germany). Poly(styrene/divinylbenzene) resin XAD-4 (from Sigma, St. Louis, MO, USA) was purified by washing with NaOH (1 mol·L^{-1}), followed by HCl (1 mol·L^{-1}), H_2O and CH_3OH/CH_2Cl_2 (1:10), and finally drying in vacuum at about 60°C before use. De-ionized eluent water was prepared by passing distilled water through a Millipore Milli-RO60 ultrapure water purification system (from Milliport, Milford, MA, USA). Methanol and acetonitrile were also used as eluents and were of LC grade. All other chemicals were either of analytical-reagent or reagent grade.

RESULTS AND DISCUSSION

The prepared cryptand resin was identified by infrared spectrophotometry with 1638 (N—H), 1280 (C—N), and 1100 cm^{-1} (C—O). The maximum adsorption capacity of the cryptand resin, deduced from elemental analysis, was about 0.73 mmol/g. The real exchange capacity of the cryptand resin, estimated from the adsorption of *cis*-butenedioate anion, was about 4.6 × 10^{-3} meq/g.

The cryptand resin packed IC (ion chromatography) column was first applied to separate various carboxylate anions. It is well known that cryptand can form stable complexes with various metal ions (2,3), but it cannot form a complex with anions. However, cryptand can be protonated in the presence of H^+ or acids, and the protonated cryptand can then form stable complexes with various anions as shown in Fig. 2. Thus, after protonation, the prepared cryptand resin can be applied as an anionic exchanger for the separation

(1) Protonation



(2) Complexation

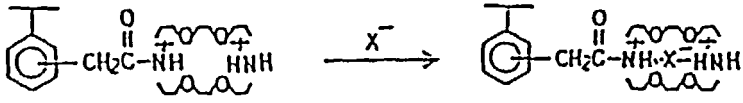


FIG. 2 Protonation and complexation of the cryptand.

of anions. As expected, after protonation with 0.01 M HNO_3, the cryptand stationary phase was protonated and successfully applied as an anionic exchanger to separate various carboxylate anions as shown in Fig. 3. The order of elution for these carboxylate anions is $HCOO^-$ (first) > CH_3COO^- > $CH_3CH_2COO^-$ > $CH_3CH_2CH_2COO^-$ (last) on the protonated cryptand column. The larger carboxylate ions, e.g., $CH_3CH_2COO^-$ and $CH_3CH_2CH_2COO^-$, have a greater retention time in the column. The larger carboxylate anion with more CH_2 groups has a stronger hydrophobic interaction and a better charge-stabilizing effect exerted by the inductive effect of the methylene group to the protonated cryptand, which probably leads to a stronger attraction between protonated cryptand and the anion, resulting in a greater retention in the cryptand column.

The height equivalent of theoretical plate (HETP) and the theoretical number of plates (N) of the cryptand column for various carboxylate anions were calculated and are shown in Table 1. The average HETP and N values of the cryptand column for these carboxylate anions are 0.0931 mm and 3313.01 plates, respectively.

The cryptand column was also successfully employed to separate the geometric isomers of carboxylates, e.g., *trans*-butenedioate (fumarate anion) and *cis*-butenedioate (maleate anion), as shown in Fig. 4. *trans*-Butenedioate anion showed a shorter retention time than *cis*-butenedioate anion. Considing the steric effect, *cis*-butenedioate anion can be expected to be used as a bidentate ligand for the protonated cryptand while *trans*-butenedioate anion is always applied as a monodentate ligand. In general, the bidentate ligand can

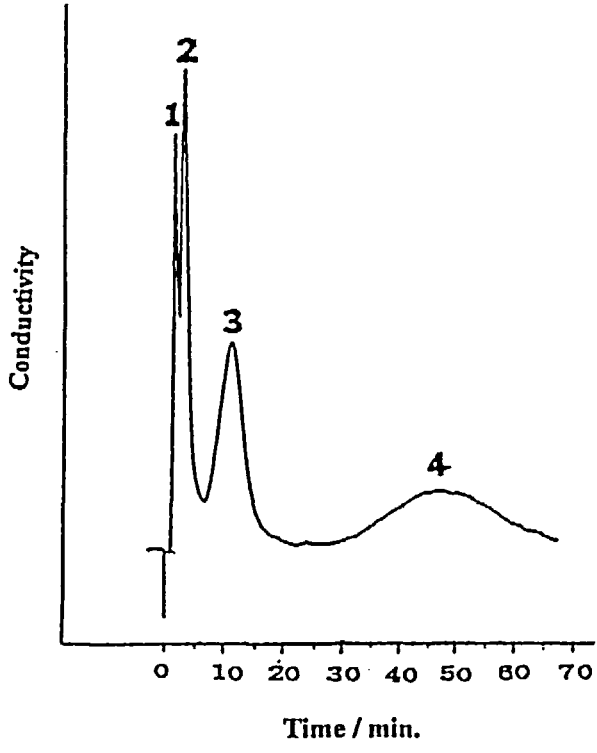


FIG. 3 Separation of carboxylate anions, (1) $HCOO^-$ (37 ppm), (2) CH_3COO^- (50 ppm), (3) $CH_3CH_2COO^-$ (104 ppm), and (4) $CH_3(CH_2)_2COO^-$ (239 ppm), with the protonated cryptand column. Eluent: H_2O. Flow rate: 1.5 mL/min. Detector: conductivity detector.

TABLE 1
Height Equivalent of Theoretical Plate (HETP) and Theoretical Number of Plates (N) of the Cryptand Column for Various Carboxylate Anions

Carboxylate anions	N	HETP (mm)
$HCOO^-$	3618.00	0.0829
CH_3COO^-	3939.58	0.0762
$CH_3CH_2COO^-$	3179.97	0.0943
$CH_3(CH_2)_2COO^-$	2514.47	0.1190
Average	3313.01	0.0931

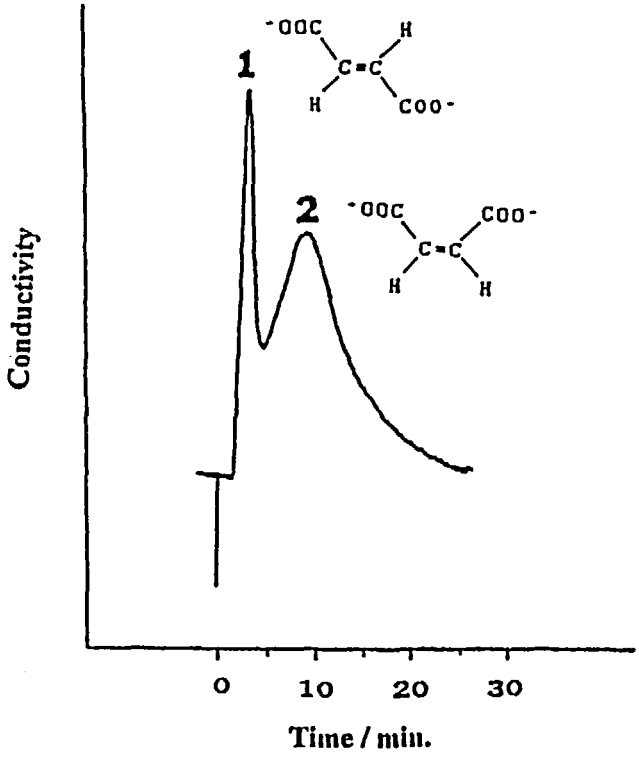


FIG. 4 Separation of (1) *trans*-butenedioate (69 ppm) and (2) *cis*-butenedioate (275 ppm) with the protonated cryptand column.

form more stable complexes with ions such as protonated cryptand than the monodentate ligand. As expected, *cis*-butenedioate anion seems to form a more stable complex with protonated cryptand and shows a longer retention time than *trans*-butenedioate anion.

As mentioned above, before protonation the neutral cryptand can form complexes with metal ions. As a result, the neutral cryptand column can also be used as a cation exchanger for the separation of cations. As shown in Fig. 5, Ca^{2+}, Sr^{2+} and Fe^{2+}, Co^{2+} can be separated at pH 7 by the neutral cryptand column. The elutions of these metal ions are in the orders 1) $Ca^{2+} > Sr^{2+}$ and 2) $Fe^{2+} > Co^{2+}$, as is the case for a common cation exchanger (20, 21) such as polystyrene/divinylbenzene sulfonate. Thus, the attraction between the cryptand and the ion is electrostatic.

The cryptand IC column can be alternately and repeatedly used as both an anion exchanger and a cation exchanger. As shown in Fig. 6(a), at pH 2 the

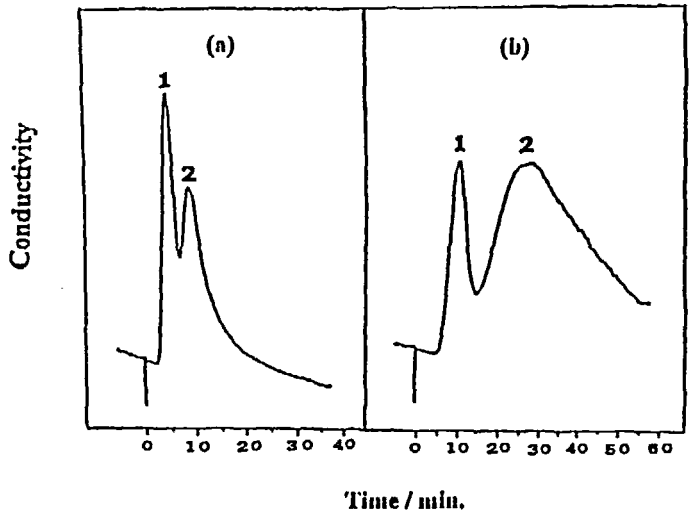


FIG. 5 Separations of various metal ions: (a) (1) Ca^{2+} (100 ppm) and (2) Sr^{2+} (150 ppm), and (b) (1) Fe^{2+} (50 ppm) and (2) Co^{2+} (125 ppm) with the cryptand column.

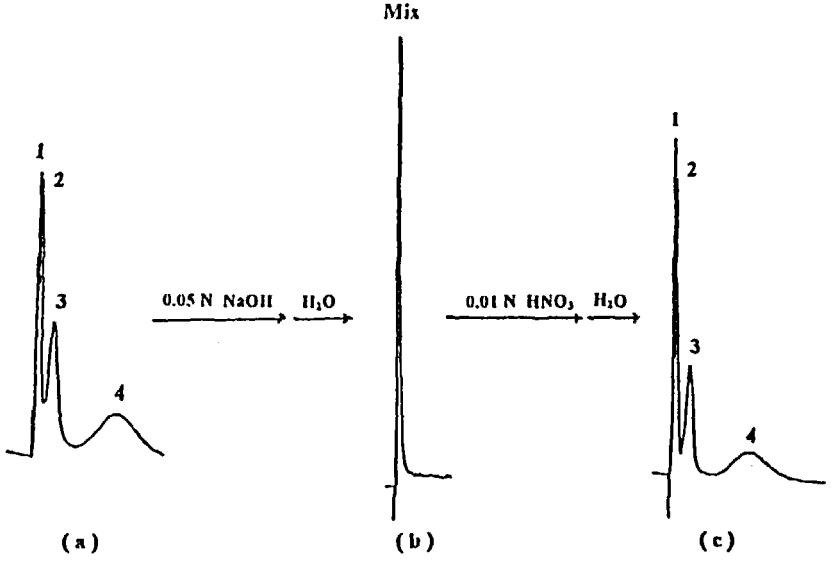


FIG. 6 Separations of sodium carboxylates on the cryptand resin with (a) protonation, (b) deprotonation, and (c) reprotonation. (1) HCOONa, (2) CH_3COONa, (3) CH_3CH_2COONa, and (4) $CH_3(CH_2)_2COONa$. Mix = mixture of HCOONa, CH_3COONa, CH_3CH_2COONa, and $CH_3(CH_2)_2COONa$.

cryptand can be protonated, and the protonated cryptand column can be applied as an anion exchanger for the separation of these carboxylate anions in water. After basification with NaOH (0.05 M) solution, the protonated cryptand can be deprotonated and changed to a neutral cryptand, and the neutral cryptand column can be employed as a cation exchanger to adsorb the cations. By using the neutral cryptand column to separate a mixture of various sodium carboxylates in water, as shown in Fig. 6(b), only one peak was observed because there was only one kind of cation (Na^+) in the solution. However, the cryptand column can be changed once again to an anion exchanger by acidification and reprotonation of the cryptand with HNO_3, and the protonated cryptand column can be applied to separate these carboxylate anions again (Fig. 6c).

The eluent's effect on cryptand column performance was also investigated. The composition of the eluent is an important factor in the separation of ions on an ion chromatograph. In general, electrolytes are used as eluents in common ion chromatography, and therefore a suppressor column is necessary for removal of the electrolytes and reduction of the signal-to-noise ratio. As shown by Fig. 3, these carboxylate anions can be separated by a protonated cryptand column using H_2O as the eluent. A major advantage of a cryptand IC column is that it makes use of a suppressor column and of electrolytes as eluents unnecessary. However, it is well known that the stability of a complex between an ion and cryptand or crown ether is significantly influenced by the solvent (22, 23). The solvent effect is an important factor in the separation of carboxylate anions. The employment of a water/organic mixed solvent, e.g., methanol/water or acetronitrile/water, results in poor separation of these carboxylate anions as shown in Fig. 7. Increased methanol or acetonitrile in the mixed solvent obviously leads to poorer separation. This seems to indicate

FIG. 7 Concentration effect of methanol in H_2O/MeOH mixed solvent on the separation of carboxylate anions: (a) H_2O, (b) 20%, (c) 40%, (d) 60%, (e) 80% (v/v) MeOH and (f) MeOH. (1) $HCOO^-$, (2) CH_3COO^-, (3) $CH_3CH_2COO^-$, and (4) $CH_3(CH_2)_2COO^-$.

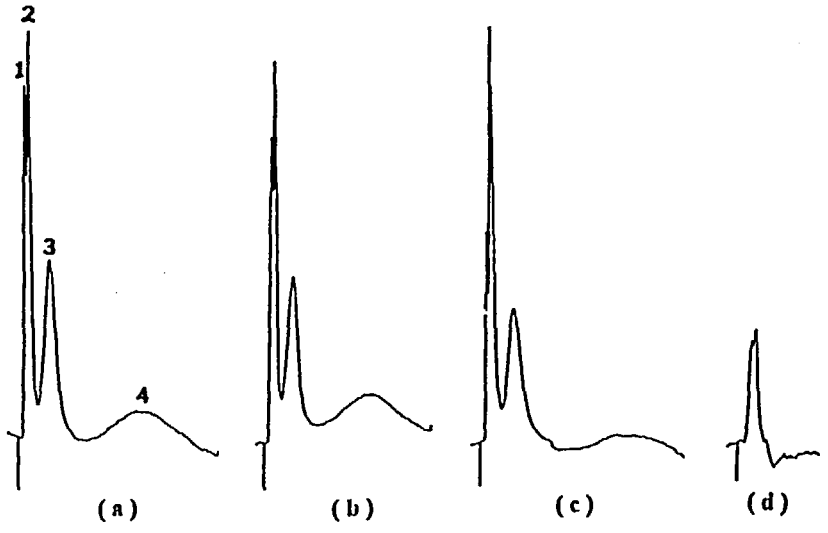


FIG. 8 pH effect on the separation of carboxylate anions at (a) pH 6.3, (b) pH 5.7, (c) pH 4.9, and (d) pH 4.0. (1) $HCOO^-$, (2) CH_3COO^-, (3) $CH_3CH_2COO^-$, and (4) $CH_3(CH_2)_2COO^-$.

that water is a much better solvent than methanol or acetonitrile. In water, a larger carboxylate anion such as $CH_3(CH_2)_2COO^-$ is expected to have better complexing ability with the cryptand and worse solvation with water than smaller carboxylates such as $HCOO^-$. This leads to better adsorption of larger carboxylate ions, resulting in good separation. However, in organic solvents, a larger carboxylate anion is expected not only to have complexing ability with a cryptand but also to have better solvation with the organic solvent than a smaller carboxylate anion. Thus, it is likely that these carboxylate anions will have a similar trend [$CH_3(CH_2)_2COO^- > CH_3CH_2COO^- > CH_3COO^- > HCOO^-$] of solvation and complexation, and therefore a similar degree of adsorption of each carboxylate anion on the cryptand column, and a poor separation will result.

The effects of pH, temperature, and flow rate were also investigated. As illustrated in Fig. 8, in the eluent pH range 6.3–4.9 the separation of carboxylate anions did not vary significantly, but at pH $\leqq$ 4.0 the separation and signals of carboxylate anions were drastically worse. This could be due to protonation of the carboxylate anion ($RCOO^-$) at pH $\leqq$ 4.0, resulting in a loss of the complexing ability of the carboxylate anion with the protonated cryptand resin. As mentioned above, the cryptand resin has complexing ability with carboxylate anions at pH $<$ 7.0 but not at pH $\geqq$ 7.0. Therefore, the separation of carboxylate anions should be carried out in the 7.0–4.0 pH range.

An increase in column temperature results in 1) a decrease in retention time, 2) a decrease in peak width, 3) an increase in peak height as shown in Fig. 9, and 4) an increase in column resolution (Fig. 10). It is well known (24) that increased temperature can cause an increase in the diffusion rate of ions and a decrease in the viscosity of the mobile phase and subsequent decreases in peak width. Meanwhile, increased temperature generally leads to a decrease in the adsorption of ions on the resin, which results in a decrease

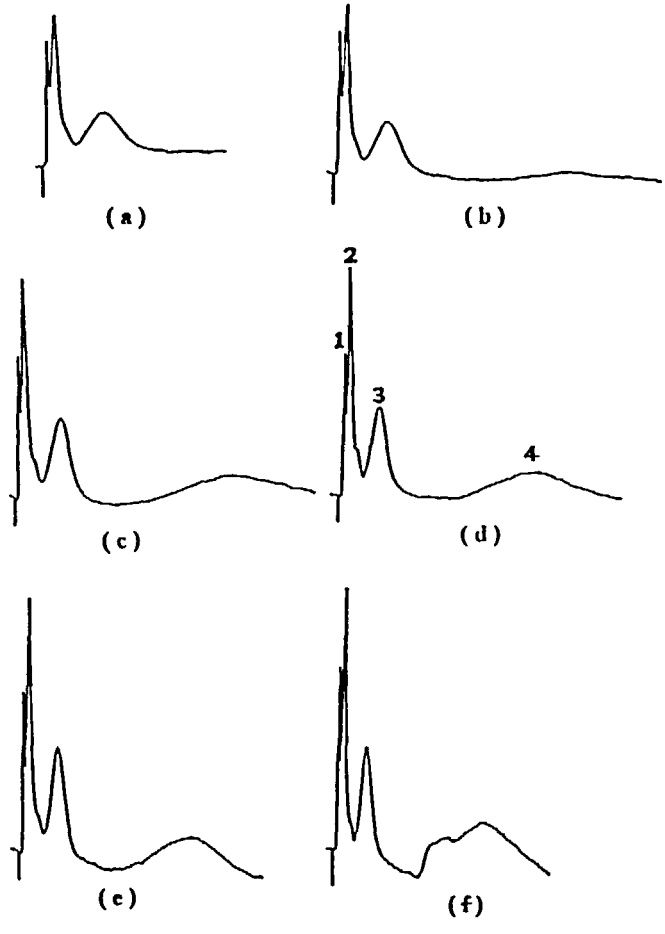


FIG. 9 Effect of temperature on the separation of carboxylate anions at (a) 5°C, (b) 10°C, (c) 20°C, (d) 25°C, (e) 30°C, and (f) 35°C. (1) $HCOO^-$, (2) CH_3COO^-, (3) $CH_3CH_2COO^-$, and (4) $CH_3(CH_2)_2COO^-$.

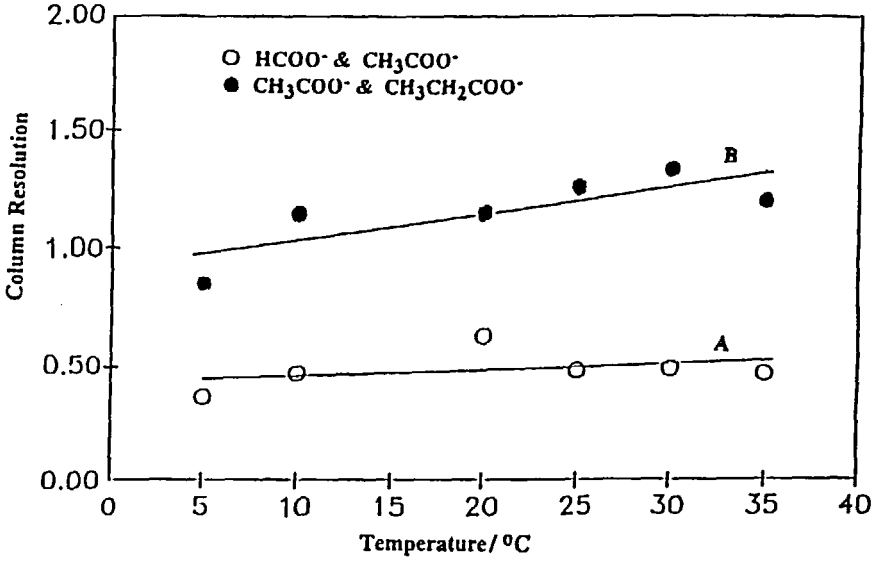


FIG. 10 Temperature effect on column resolution for various carboxylate anions.

in the retention time of ions. Furthermore, the conductivity of ions can be increased through the elevation of column temperature, which leads to an increase in the peak height of each anion. The slight improvement of column resolution at higher column temperature may be due to the decrease of peak width predicted by Eq. (3).

The effect of flow rate on carboxylate anion separation was also investigated. According to the Van Deemter equation (25):

$$\text{HETP} = A + (B/\upsilon) + C\upsilon$$

HETP can be controlled, by using the flow rate ($\dot{\upsilon}$) of the eluent. As shown in Fig. 11, the increase in flow rate causes a linear increase in HETP. This result seems to indicate that the HETP of carboxylate anions is dependent upon both the A and C terms, and that the B term in the Van Deemter equation seems negligible, which results in a linear increase of the HETP with increasing flow rate. The A and C terms were evaluted to be 0.35 cm and 0.45 cm·min/mL for CH_3COO^- and 0.45 cm and 0.33 cm·min/mL for $HCOO^-$ from the intercepts and the slopes of the curves in Fig. 11. In general, an increase of HETP indicates a poorer separation and resolution. As expected, the column resolution between two carboxylate anions becomes poorer with increasing flow rate of the eluent, as shown in Fig. 12.

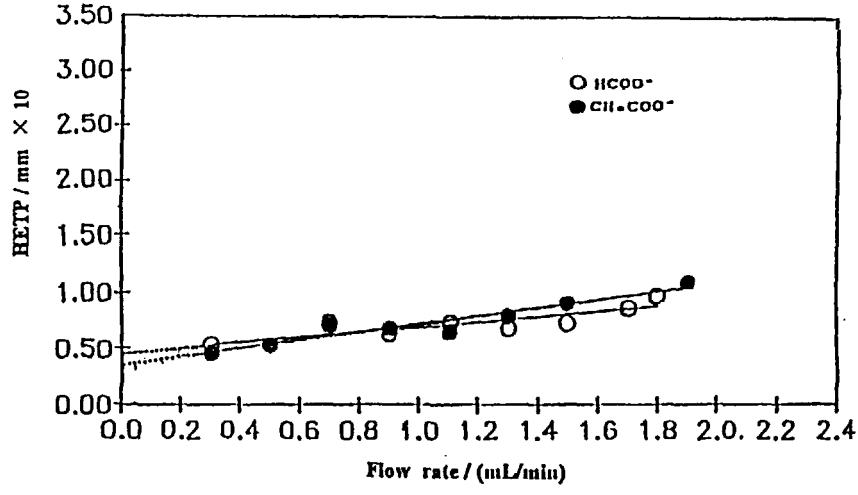


FIG. 11 Plot of HETP against flow rates.

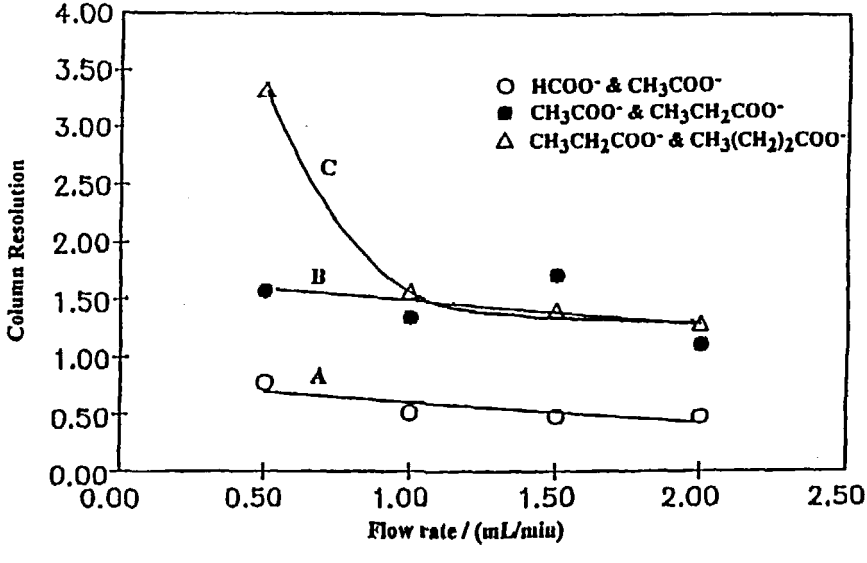
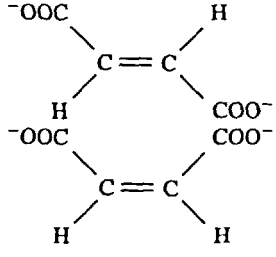


FIG. 12 Column resolution for carboxylate anions at various flow rates.

TABLE 2
Reproducibility of Carboxylate Anion Determination

Anion	Concentration (ppm)	No. of sample	RSD (%)
HCOO-	100	5	0.134
CH_3COO^-	100	5	0.131
	138.5	5	0.064
	138.5	5	0.264

Finally, the stability and the reproducibility of the cryptand ion chromatographic stationary phase for separations of these carboxylate anions were also investigated. As shown in Table 2, the quite good relative standard deviation (RSD, %) found in each case indicates that the cryptand ion chromatographic phase exhibits good stability and repeatability.

In conclusion, the cryptand ion chromatographic column can be applied as an anionic exchanger for the separation of carboxylate anions after protonation at pH < 7 and can be changed to a cation exchanger after deprotonation in a basic solution for the separation of metal ions. The protonated cryptand column exhibits good resolution for various carboxylate anions and allows even the geometric isomers of carboxylate anions to be separated. In addition, the cryptand ion chromatographic column demonstrates good reproducibility and stability.

ACKNOWLEDGMENT

The authors express their appreciation to the National Science Council of the Republic of China in Taiwan for financial support.

REFERENCES

1. C. J. Pederson, *J. Am. Chem. Soc.*, *89*, 7017 (1969).
2. I. M. Kolthoff, *Anal. Chem.*, *51*, 1R (1979).
3. B. Dietrich, J. M. Lehn, and T. P. Sauvage, *Tetrahedron Lett.*, *288*, 55 (1969).
4. J. Christensen, D. J. Eatough, and T. M. Izatt, *Chem. Rev.*, *74*, 351 (1974).

5. H. K. Frensdorff, *J. Am. Chem. Soc.*, *93*, 4684 (1971).
6. J. S. Shih, *J. Chin. Chem. Soc.*, *39*, 551 (1992).
7. K. Kimura, J. Maeda, and J. Shono, *J. Electroanal. Chem.*, *95*, 91 (1979).
8. J. S. Shih, *J. Chin. Chem. Soc.*, *41*, 309 (1994).
9. E. Blasius, K. P. Janzen, H. Luxenburger, V. B. Nguyen, H. Klotz, and J. Stockemer, *J. Chromatogr.*, *167*, 307 (1978).
10. L. M. Tsay, J. S. Shih, and S. C. Wu, *Analyst*, *108*, 1108 (1983).
11. S. R. Sheen and J. S. Shih, *Ibid.*, *117*, 169 (1992).
12. E. Graf and J. M. Lehn, *J. Am. Chem. Soc.*, *98*, 6403 (1976).
13. J. Cheney, J. P. Kintzinger, and J. M. Lehn, *Nour. J. Chim.*, *2*, 488 (1978).
14. J. M. Lehn, *J. Am. Chem. Soc.*, *103*, 6044 (1981).
15. F. Schmidtchen and G. Muller, *J. Chem. Soc., Chem. Commun.*, *132*, 101 (1986).
16. S. J. Chen and J. S. Shih, *J. Chin. Chem. Soc.*, *38*, 211 (1991).
17. D. A. Skoog and J. J. Leary, *Principles of Instrumental Analysis*, 4th ed., Harcourt Brace Jovanovich, Orlando, FL, 1992, p. 587.
18. *Ibid.*, p. 586.
19. *Ibid.*, p. 592.
20. H. Small, T. S. Stevens, and W. C. Bauman, *Anal. Chem.*, *47*, 1801 (1975).
21. F. C. Smith and R. C. Chang, *The Practice of Ion Chromatography*, Wiley, New York, NY, 1983, p. 15.
22. H. J. Buschmann, *Inorg. Chem.*, *120*, 125 (1986).
23. J. S. Shih and A. I. Popov, *Ibid.*, *19*, 1689 (1980).
24. R. Ungro, B. E. Haj, and J. Smid, *J. Am. Chem. Soc.*, *98*, 598 (1979).
25. G. D. Christian and J. E. O'Reilly, *Instrumental Analysis*, 2nd ed., Allyn and Bacon, Boston, MA, 1978, p. 669.

Received by editor November 5, 1996
Revision received October 1997