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Silica-bonded calixarenes in chromatography II. Chromatographic retention of metal ions and amino acid ester hydrochlorides

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Abstract

The chromatographic behaviour of alkali and alkaline earth metal ions on a silica-bonded macrocyclic calix[4]arene tetradiethylamide phase is reported. Selective retention of Na^+ over other alkali metal ions and of Ca^{2+} over Mg^{2+} ions is found using water as the mobile phase and conductivity detection. A series of amino acid ester hydrochlorides are shown to be retained in order of their hydrophobicity on a silica bonded calix[4]arene tetraester phase with aqueous mobile phases containing lithium perchlorate and acetonitrile. Retention of metal ions and organic solutes on these new silica-bonded functionalised calixarene phases is dependent on the organic modifier concentration.

Keywords: Stationary phases, LC; Alkali metals; Alkaline earth metals; Amino acid ester hydrochlorides; Metal ions

1. Introduction

The host–guest interactions of calix[*n*]arenes with a variety of neutral and ionic species have been widely reported. Calix[*n*]arenes are cyclic oligomers composed of phenolic units linked by methylene bridges at positions ortho to the hydroxyl groups. These compounds may contain four to eight aryl moieties arranged in a macrocyclic array with a central cavity [1]. Derivatisation of the phenolic groups has produced a variety of functionalised calixarenes which show selective ionophoric properties towards certain guest species. The host–guest interaction is determined by the overall macrocyclic structure, most importantly by the cavity size but also by the nature of the functional groups which act as the binding sites.

The ionophoric properties of functionalised calixarenes have been clearly demonstrated using NMR spectroscopy and by liquid–liquid extraction studies [2]. In particular, the conversion of p-*tert.*-butylcalix[4]arene and *p-tert.*-butylcalix[6]arene into acetic esters, ketones and amides results in ionophoric activity [3,4]. The phase transfer activity of these compounds has been demonstrated for the extraction of metal picrates from water into dichloromethane.

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The tetrameric calixarene esters, ketones and amides show a selective ability to extract Na^+ while the hexameric calixarenes have higher efficiencies for Cs^+ ions. These selective complexation properties have been successfully exploited in the construction of ion-selective electrodes [5,6] and in the development of chemically-modified voltammetric sensors [7].

The separation of alkali and alkaline earth ions on chemically-bonded crown ether stationary phases, using simple water–methanol mobile phases, has previously been reported [8–10]. The application of silica-bonded calixarene phases for ion separations or pretreatment offers exciting possibilities, in view of the established control of selectivity for these ions that is possible through lower rim functionalisation. A silica-bonded calix[4]arene tetraester phase has been shown to have enhanced chromatographic selectivity for Na^+ over other alkali metal ions [11]. In this paper, the ion retention characteristics of the silica-bonded tetrameric calixarene tetradiethylamide phase (see Part I [12]) for alkali and alkaline earth metal ions are investigated using chromatography.

Previous reports on the separation and analysis of organic hosts using calixarene derivatives are also scarce. In the main, research reports have concentrated on the use of the water soluble calix[6]arene–*p*-sulphonate in the modification of selectivity for substituted phenols in capillary electrophoresis [13] and reversed-phase liquid chromatography [14]. However, extraction, potentiometric and NMR evidence from many sources strongly indicates selective inclusion of amines in calixarene cavities [15,15,17–19]. Of particular interest is the interaction between an underivatised calixarene, *p*-allylcalix[4]arene and *tert.*-butylamine in acetonitrile solution. Proton NMR evidence has indicated the formation of an endo-calix complex where the protonated amine guest is accommodated in the negatively charged calixarene cavity [16,17]. A selective transport of amino acid esters through a chloroform membrane by a calix[6]arene based hexaester carrier has been reported. Transport efficiency was found to be closely related to the hydrophobicity of the amino acid esters studied and it is also postulated that the ammonium group of the guest is anchored in the carrier cavity forming an endo-calix complex [20].

Potentiometric discrimination of primary organic amines having no substituent adjacent to the amine group has been possible using membrane electrodes based on hexaesters of calix[6]arene. Both proton NMR evidence and potentiometric studies have indicated an accommodation of primary amine guests in the cavity of the calix[6]arene hexaesters with a tripodal hydrogen bonding interaction between the ammonium moiety of the guest and the carbonyl groups at the calixarene binding site. The encapsulation of primary amines and not secondary or tertiary amines in the calixarene cavity indicates a sterically controlled selectivity. The electrodes also displayed a selectivity which reflected simple lipophilicity of the guests [21,22]. In this paper, as an example illustrating the multimodal potential of these new silica-bonded calixarenes phases, the chromatographic behaviour of a series of amino acid ester hydrochlorides is reported using a calix[4]arene tetraester stationary phase.

2. Experimental

2.1. Chemicals and reagents

Silica (Nucleosil, 5 μm particle size, 100 Å) was purchased from Macherey-Nagel (Düren, Germany). Lithium perchlorate, benzamide, benzophenone and biphenyl were purchased from BDH Chemicals (Poole, UK). HPLC grade methanol and acetonitrile and AnalaR grade toluene were purchased from Merck (Darmstadt, Germany). All alkali metal salts were AnalaR grade from BDH (Poole, UK). The hydrochloride salts of L-phenylalanine methyl ester (PME), L-phenylalanine ethyl ester (PEE), L-alanine benzyl ester (ABE), β-alanine ethyl ester (AEE) and D-tryptophan methyl ester (TME) were purchased from Sigma (Poole, Dorset, UK). The hydrochloride salt of L-aspartyl–L-phenylalanine methyl ester (ASP) was obtained from Aldrich Chemical Co. (Dorset, UK).

2.2. Instrumentation

For ion chromatography, the system consisted of a Dionex metal free pump and injection system, plumbed with PTFE tubing. The injection was pneumatically driven, with a loop volume of 75 μl,

unless otherwise stated. The conductivity detector used was a Dionex CDM II utilising a Dionex conductivity cell (8 μl volume) and incorporating temperature compensation facilities. Empty PEEK columns (7 cm×4.0 mm I.D.) were obtained from Dionex and slurry packed with the silica-bonded calix[4]arene tetraamide phase. An Elgastat water purification system provided water for ion chromatography with a resistivity greater than 15 Mohm/cm.

For organic analysis, the Shimadzu chromatographic system consisted of a SCL-8A system controller, a LC-8A preparative LC pump unit, a UV spectrophotometric detector SPD-6A module and a C-R4A chromatopac data processor. A stainless steel column (7 cm×4.5 mm I.D.) slurry packed with the silica-bonded calix[4]arene tetraester stationary phase was used in the analysis. A guard column (1.8 cm×1.5 I.D.) packed with the same material was also incorporated in the system.

2.3. Synthesis of the triethoxysilane derivatives of calix[4]arenes

p-Allylcalix[4]arene was prepared according to the reported procedure [23,24] and was converted into it's ethyl acetate derivative by refluxing with ethyl bromoacetate in acetone in the presence of anhydrous potassium carbonate as described previously [4]. Following hydrolysis to the carboxylic acid, *p*-allylcalix[4]arene tetraacid was treated with oxalyl chloride to afford *p*-allylcalix[4]arene tetraacid chloride, which on further treatment with N,N-diethylamine in tetrahydrofuran was converted to the diethylamide.

Two types of triethoxysilane derivatives were prepared, differing in the linkage between the calixarene and the triethoxysilane group (see reaction scheme, Fig. 1): (i) *n*-Propyl linkage: conversion of the *p*-allylcalix[4]arene derivative to the desired silicon derivative involving the hydrosilation addition reaction of $(CH_3CH_2O)_3SiH$ to the double bond of the *p*-allylcalix[4]arene derivative in toluene using a hexachloroplatinic acid catalyst at 120°C (Fig. 1a); (ii) di-*n*-Propyl sulphide linkage: the *p*-allylcalix-[4]arene derivative was treated with mercaptopropyltriethoxysilane at 70°C for one hour in the presence of cumene hydroperoxide (CHP, free radical source

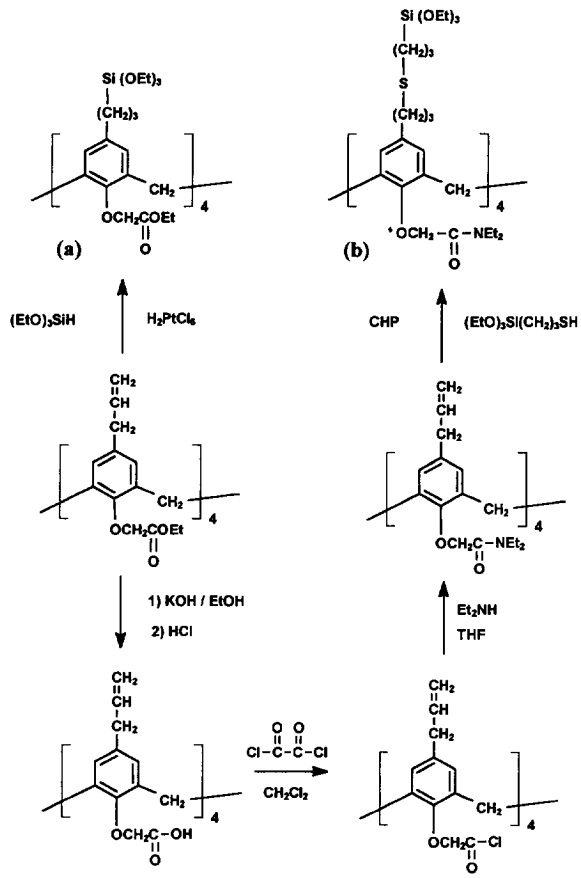

Fig. 1. Reaction scheme for for synthesis of triethoxysilyl derivatives of (a) tetraethyl *p*-*n*-propylcalix[4]arene tetraacetate and (b) *p*-di-*n*-propylsulphidecalix[4]arene tetraacetyldiethylamide.

for thiolene addition) to yield the triethoxysilane derivative (Fig. 1b).

Immobilisation of the tetraester and the tetradiethylamide calixarenes onto silica was carried out as reported in the preceding paper [12].

3. Chromatographic procedures

3.1. Ion chromatography with water eluent

The chromatographic selectivity for alkali metal and alkaline earth metal ions was examined at room temperature by injection of standard aqueous solutions, prepared in the concentration range from 0.1 m*M*–10 m*M*, onto the calix[4]arene tetraamide phase

with water as the mobile phase. Injections of methanol were used to determine the t_0 value. Methanol in different concentrations was added to the mobile phase and its influence on the retention determined. The effect of various anions on the sodium retention was also examined.

3.2. Liquid chromatography of organic solutes

A solution of benzamide (6.1×10^{-5} *M*), benzophenone (7.68×10^{-5} *M*) and biphenyl (1.30×10^{-4} *M*) was prepared in MeOH–H_2O (70:30, v/v) and injections ($n\geq5$) of the mixture were made onto the calix[4]arene tetraester phase, with aqueous mobile phases containing methanol as the organic modifier. The injection volume was 20 μl, the flow-rate was 1 ml min^{-1} and spectrophotometric detection was at 254 nm.

Aqueous solutions of the hydrochloride salts of six amino acid esters, L-phenylalanine methyl ester, L-phenylalanine ethyl ester, L-alanine benzyl ester (each at 1×10^{-4} *M*), β-alanine ethyl ester (5×10^{-3} *M*), D-tryptophan methyl ester (1×10^{-5} *M*) and L-aspartyl–L-phenylalanine methyl ester (5×10^{-5} *M*) were injected onto the column. All the chromatographic standards were prepared in doubly distilled water. The analysis was carried out using an injection volume of 20 μl, a flow-rate of 1 ml min^{-1} and spectrophotometric detection at 210 nm. Aqueous mobile phases containing lithium perchlorate and acetonitrile were filtered under vacuum through 0.45-μm filters on a Millipore filtration unit. This procedure and subsequent sonication degassed the mobile phases. Repetitive injections ($n\geq5$) were made for all solutions and mixtures.

4. Results and discussion

The complexing ability of free calix[4]arenes functionalised with ligating ester and amide groups have been determined by extraction and stability constant measurements [25]. While selectivity for Na^+ ions is observed in both cases, the diethylamide exhibited substantial complexation of the alkaline earths; in particular, it is reported to display the highest selectivity for Ca^{2+} over Mg^{2+} for a neutral carrier. In the previous paper, the use of solid state NMR in the characterisation of silica bonded functionalised calixarenes is demonstrated but a key question is whether or not the complexation selectivity would apply on the bonded solid phases. Chromatography can be a useful means of demonstrating the selectivity of such new materials. Previous indications with silica bonded crown ethers and with the calix[4]arene tetraester are that ion separations are possible [11]. In the present work using conductivity detection and with water only as the mobile phase, sodium ions are retained significantly longer than all the other alkali metal ions on the silica-bonded calix[4]arene tetradiethylamide column. While sharp peaks very close to the t_0 are obtained on injections of LiCl, KCl and CsCl, NaCl has a different chromatographic behaviour, is retained and shows fronting. Capacity factors obtained on injection of 10 m*M* standards of alkali metal and alkaline earth salts are given in Table 1. A mixture of 5 m*M* NaCl and 5 m*M* KCl is clearly separated (Fig. 2). If water–methanol mixtures are utilised instead of pure water as the mobile phase, the retention of NaCl increases with the rise of methanol fraction in the eluent. This is illustrated in Fig. 3, where the separation factor and capacity factors for NaCl and KCl are plotted against % methanol. The separation factor for NaCl over KCl changes from 2.3 with water to 6.0 with 40% methanol. The retention times of LiCl, KCl and CsCl are independent of the methanol content. However, peak fronting becomes more distinct for NaCl as retention increases. Interestingly, when varying concentrations of NaCl in water (0.1–10.0 m*M*) were injected using a mobile phase of 40% methanol and a flow-rate of 1.0 ml min^{-1}, the capacity factors of LiCl, KCl and

Table 1
Capacity factors (k') for salts on silica-bonded calix[4]arene tetraamide column (pure water mobile phase)

Cation (XCl_n) X	k'	Anion (NaY_n) Y	k'
Li^+	0.57	Cl^-	1.29
Na^+	1.29	Br^-	0.78
K^+	0.57	SCN^-	0.11
Cs^+	0.57	SO_4^{2-}	0.60
Mg^{2+}	0.47	ClO_4^-	0.83
Ca^{2+}	4.00	Ac^-	0.71
Ba^{2+}	0.51		

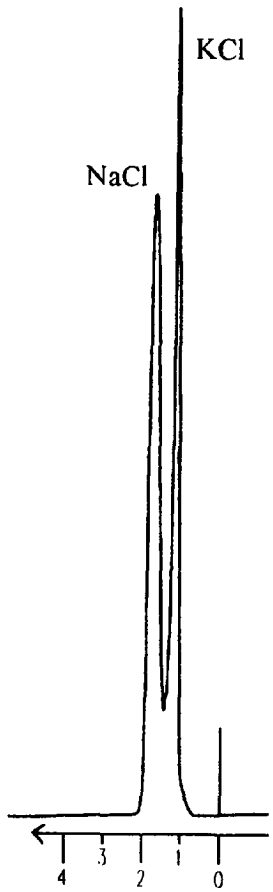

Fig. 2. Chromatographic separation of NaCl and KCl on a silica-bonded calix[4]arene tetraamide column (5 m*M* each; mobile phase, water; flow-rate, 1.0 ml/min; conductivity detection).

CsCl showed only minor increases, but the capacity factor of NaCl (and therefore the value of the separation factor too) was increased from 1.8 to 2.6 with increasing concentration. The use of water or other polar solvents as the sole component of the mobile phase in ion chromatography, can eliminate the need for electrolytes, precise mobile phase make-up and ion suppression as part of conductivity detection. As with crown ethers described earlier in the literature, water-eluent based ion chromatography is a convenient way to demonstrate the selectivity of the solid phases, a selectivity which can be modulated by suitable functionalisation of the lower rim. Apart from sample matrix effects, the anion effect on cation retention observed here, as given in Table 1 for Na^+ retention would be another practical disadvantage to the use of these phases for water eluent based ion chromatography but this could be overcome by insertion of a small anion exchange pre-column to convert anions to a suitable common cation, as suggested by Small [26].

The behaviour of Ca^{2+} on this silica-bonded calix[4]arene tetradiethylamide phase would in particular, indicate if the selectivity of the free calixarene had transferred to the solid phase. Significantly, a long retained but broad band was observed for Ca^{2+}, indicating selective retention of this alkaline earth over Mg^{2+} and Ba^{2+}, a result in keeping with stability constant data. While this work concentrates on demonstrating the selectivity of the solid-phase materials, further studies on the factors that influence selectivity and column efficiency are needed, as was the case for the first studies on bonded crown ether phases.

Silica-bonded calixarene phases would in addition to ion separations, be expected to display reversed-phase behaviour. One convenient approach, used here with the silica-bonded calix[4]arene tetraester phase (previously shown to have chromatographic selectivity for Na^+ over other alkali metals [8]), is to inject a typical standard test mixture such as benzamide, benzophenone and biphenyl, using a water–methanol mobile phase. Significant retention and a baseline separation were achieved for the components of the mixture using this new stationary phase. The dependence of log retention factor on the organic modifier content of the mobile phase was investigated for aqueous mobile phases containing 30 to 60% methanol (Fig. 4). A linear decrease in log retention factor is observed with increasing methanol content. The observed selectivity may be attributed to an interaction between the aryl moieties of the solutes and the immobilised calix[4]arene. Preliminary results indicate that further improvements in column efficiency are possible by optimisation of column packing and selection of particle size and mobile-phase composition.

In addition, following reports of selective phase transport of amino acid ester hydrochlorides using calixarenes [20], their chromatographic behaviour on this silica bonded calix[4]arene tetraester phase was investigated. Complete retention of all the amino acid esters studied except aspartame on the column was observed when a mobile phase of pure water

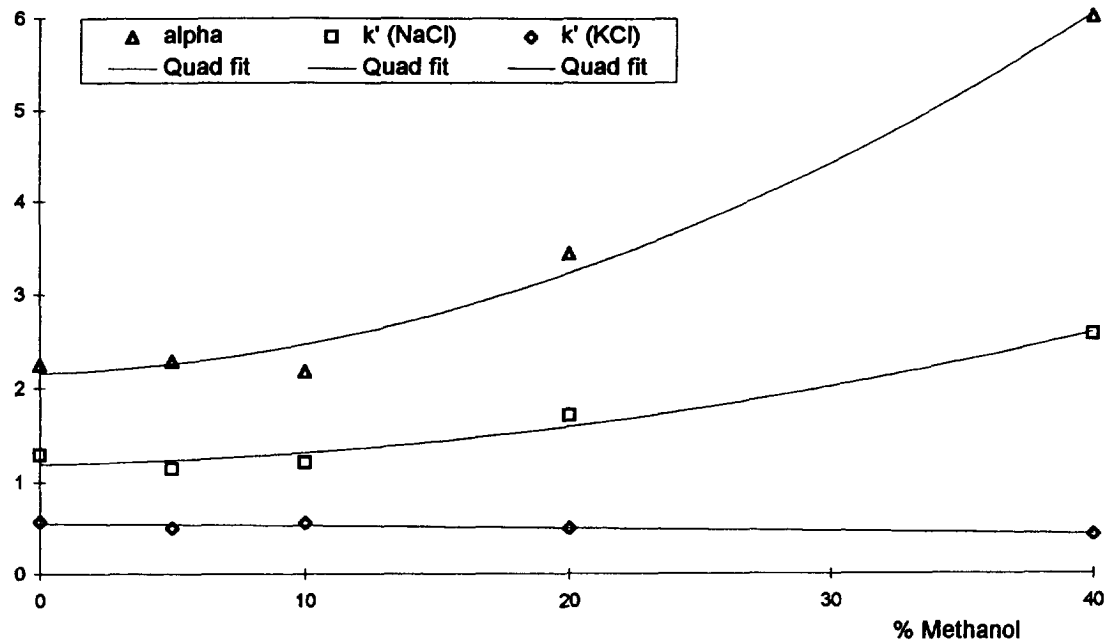

Fig. 3. Variation in capacity factors and separation factor for NaCl and KCl as a function of % methanol (5 m*M* each).

was used. On addition of 50% organic modifier (acetonitrile) to the mobile phase, elution of the esters was observed; however the peaks were broad, non-symmetrical and of low intensity. The effect of addition of lithium perchlorate to a mobile phase of 20% ACN–H_2O was examined in the present study. The dependence of retention factor on lithium perchlorate concentration in the mobile phase is shown in Fig. 5, with retention decreasing with increasing salt concentration. The addition of lithium perchlorate to the mobile phase also resulted in improved peak shape and symmetry. Retention decreased with increasing acetonitrile content of the mobile phase, when injections were made with aqueous mobile phases of 20%, 15%, 10% and 5% ACN, all with 10 m*M* lithium perchlorate. The order of retention was found to be closely related to the lipophillicity of the amino acid esters i.e. TME>PEE>ABE>PME> AEE>APM. While plots of log k' against modifier concentrations used here were not linear (Fig. 6), reversed-phase chromatographic behaviour appears dominant, a conclusion reinforced by the longer retention of phenylalanine ethyl ester over phenylalanine methyl ester. It is possible that the ammonium moiety of the amino acid esters may interact with the oxygen atoms of the ester carbonyl groups at the calixarene binding sites in an inclusion manner similar to that observed for alkali metal ions. The presence of bulky substituents at the α-carbon in the amino acid esters makes inclusion in the calixarene cavity unfavourable, as they would sterically hinder any tripodal hydrogen bonding between the amino group and the calixarene carbonyl groups. All the esters studied except β-alanine ethyl ester have bulky substituents adjacent to the amine moiety. However, β-alanine ethyl ester, with a short unbranched alkyl chain adjacent to the primary amine group, shows no evidence of enhanced retention due to amine inclusion while D-tryptophan methyl ester, heavily substituted close to the amine group, is the longest retained. The observed selectivity can be attributed to the interaction of the aryl moieties of the solutes with those on the immobilised calixarene through π–π interactions. Furthermore, tetraethyl

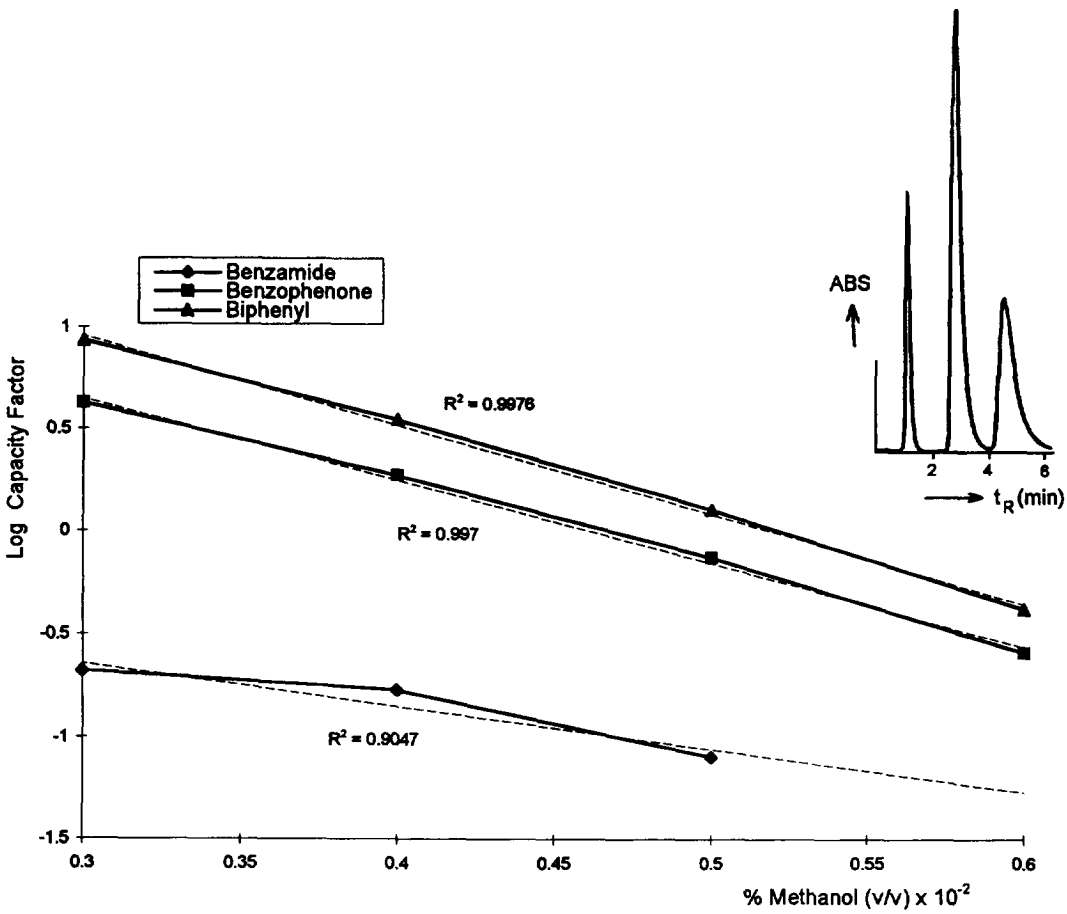

Fig. 4. Plot of log retention factors of benzamide, benzophenone and biphenyl versus the concentration of MeOH on silica-bonded calix[4]arene tetraethylacetate (flow-rate, 1 ml/min; detection at 210 nm).

p-tert.-butyl calix[4]arene tetraacetate has been reported to extract lithium picrate to a level of 15% into a dichloromethane solution in extraction studies [4]. It is possible that lithium ions in the mobile phase are complexed in the calixarene cavity thereby reducing the number of binding sites available for amino acid ester complexation, resulting in shorter elution times and a hydrophobic retention mechanism predominating. Aspartame is the shortest retained due likely to the presence of an ionised carboxylate group. Baseline separation of selected amino acid esters is possible with a mobile phase of 20% acetonitrile–water with 5 m*M* lithium perchlorate and typical separations are shown in Fig. 7. Further studies on the chromatographic properties of these new silica bonded functionalised calixarene phases are continuing.

5. Conclusion

Silica-bonded calix[4]arene tetradiethylamide stationary phases show selective retention of Na^+ over other alkali metal ions and for Ca^{2+} ions over Mg^{2+} following injection with pure water mobile phases. reversed-phase behaviour is indicated for a

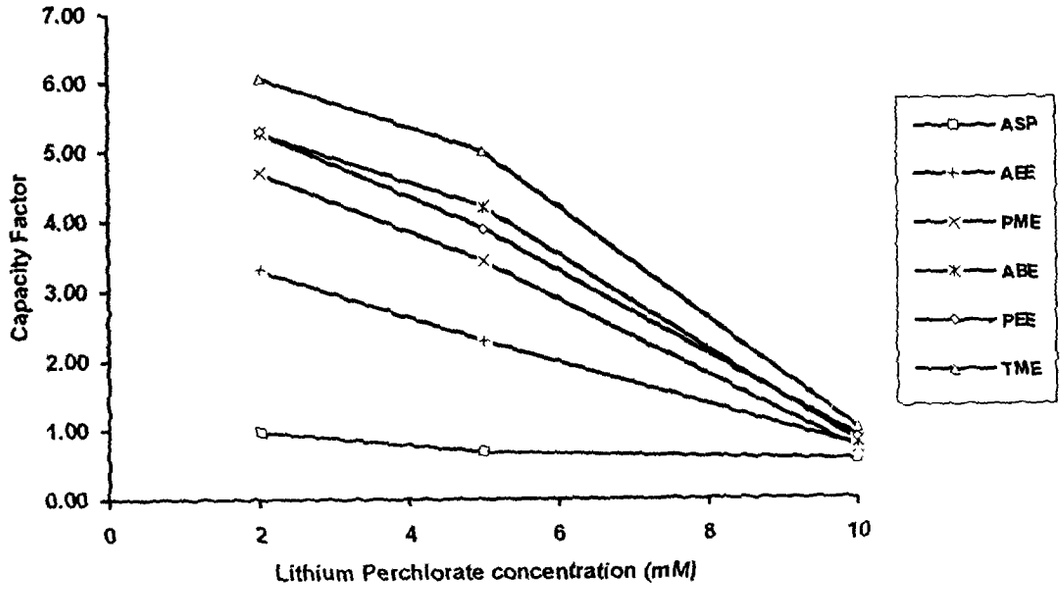

Fig. 5. Variation of retention factor of the hydrochloride salts of six amino acid esters with lithium perchlorate concentration of the mobile phase (20% ACN–H_2O).

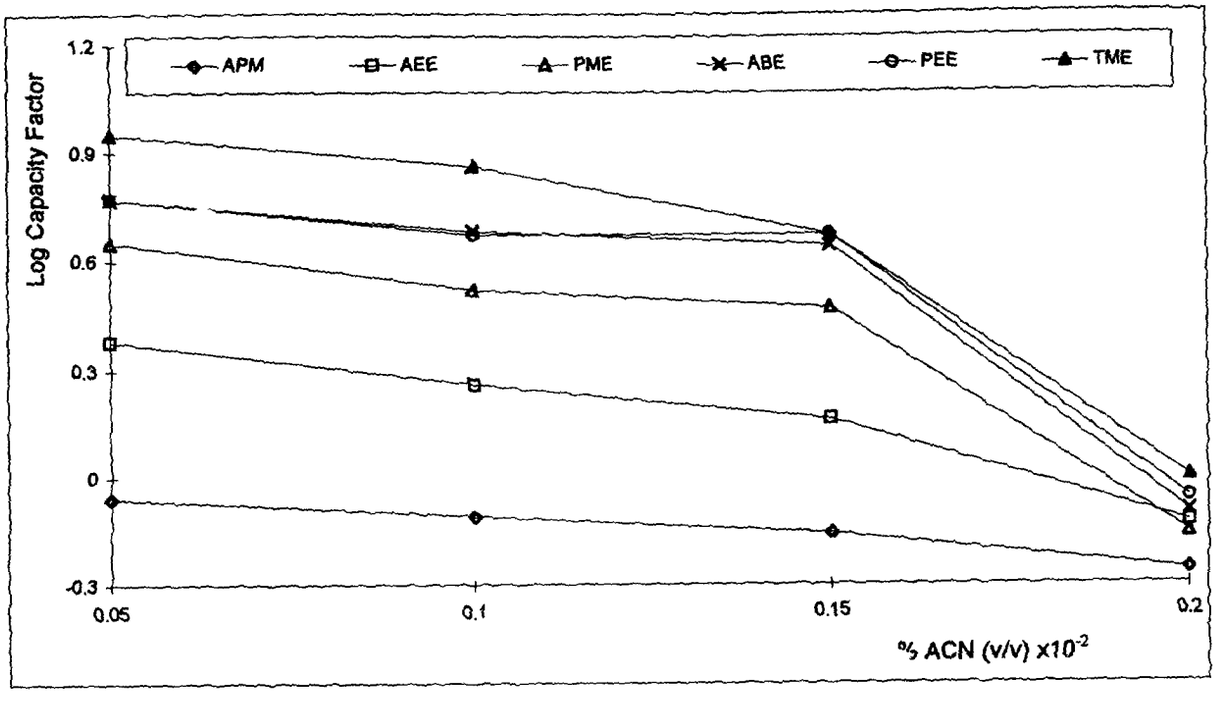

Fig. 6. Plot of log retention factors for amino acid esters hydrochlorides versus concentration of acetonitrile (10 m*M* lithium perchlorate).

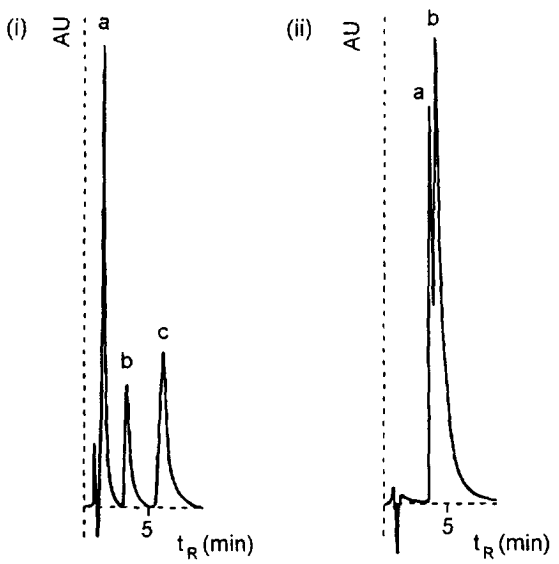

Fig. 7. Chromatographic separation of the hydrochloride salts of: (i) (a) L-aspartyl–L-phenylalanine methyl ester, (b) β-alanine ethyl ester and (c) L-tryptophan methyl ester. (ii) (a) L-Phenylalanine ethyl ester and (b) L-phenylalanine methyl ester. (Mobile phase, 20% ACN–H_2O, 5 m*M* $LiClO_4$; flow-rate, 1 ml/min.)

series of amino acid hydrochlorides on a silica-bonded calix[4]arene tetraester phase. Retention of metal ions and organic solutes vary in opposite directions with increasing organic modifier concentration. These new molecular recognition phases based on macrocyclic calixarenes show enormous potential for the tailoring of chromatographic selectivity through calixarene functionalisation and the use of mobile-phase additives.

References

[1] C.D. Gutsche, Calixarenes, in J.F. Stoddart (Editor), Monographs in Supramolecular Chemistry, Vol. 1, Royal Society of Chemistry, London, 1989.

[2] V. Bohmer and J. Vicens (Editors), Topics in Inclusion Phenomena, Calixarenes, A Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, 1990.

[3] R. Ungaro and A. Pochini, in V. Bohmer and J. Vicens (Editors), Topics in Inclusion Phenomena, Calixarenes, A Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, 1990, pp. 127–147; M.J. Schwing-Weill and M.A. McKervey, in V. Bohmer and J. Vicens (Editors), Topics in Inclusion Phenomena, Calixarenes, A Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, 1990, pp. 149–172.

[4] F. Arnaud-Neu, E.M. Collins, M. Deasy, G. Ferguson, S.J. Harris, B. Kaitner, A.J. Lough, M.A. McKervey, E. Marques, B.L. Ruhl, M.J. Schwing-Weill and E.M. Seward, J. Am. Chem. Soc., 111 (1989) 8681.

[5] D. Diamond, G. Svehla, E. Seward and M.A. McKervey, Anal. Chim. Acta, 204 (1988) 223.

[6] K. Kimura, T. Miura, M. Matsuo and T. Shono, Anal. Chem., 62 (1990) 1510.

[7] D.W.M. Arrigan, G. Svehla, S.J. Harris and M.A. McKervey, Electroanalysis, 6 (1994) 97–106.

[8] E. Blasius, K.P. Janzen, W. Klein, H. Klotz, T. Nguyen-Tien, R. Pfeiffer, G. Scholten, H. Simon, H. Stockemer and A. Oouissant, J. Chromatogr., 201 (1980) 147–166.

[9] K. Kimura, H. Harino, E. Hayata and T. Shono, Anal. Chem., 58 (1986) 2233–2237.

[10] J.S. Bradshaw, R.M. Izatt, J.J. Christensen, K.E. Krakowiak, B.J. Tarbet, R.L. Bruening and S. Lifson, J. Inclusion Phenomena and Molecular Recognition in Chemistry, 7 (1989) 127–136.

[11] J.D. Glennon, K. O'Connor, S. Srijaranai, K. Manley, S.J. Harris and M.A. McKervey, Anal. Lett., 26 (1993) 153.

[12] R. Brindle, K. Albert, S.J. Harris, C. Tröltzsch, E. Horne and J.D. Glennon, J. Chromatogr. A, 731 (1996) 41.

[13] D. Shohat and E. Grushka, Anal. Chem., 66 (1994) 747–750.

[14] J.H. Park, Y.K. Lee, N.Y. Cheong and M.D. Jang, Chromatographia, 37 (1993) 221–223.

[15] L.J. Bauer and C.D. Gutsche, J. Am. Chem. Soc., 107 (1985) 6063.

[16] C.D. Gutsche, M. Iqbal and I. Alam, J. Am. Chem. Soc., 109 (1987) 4314.

[17] C.D. Gutsche, M. Iqbal, K.S. Nam, K. See and I. Alam, Pure Appl. Chem., 60 (1988) 483.

[18] G. Görmar, K. Seiffarth, M. Schulz and C.L. Chachimbombo, J. Prakt. Chem., 333 (1991) 475.

[19] A. Danil de Namor, M.T. Garrido Pardo, L. Muñoz, D.A. Pacheco Tanaka, F.J. Sueros Velarde and M.C. Cabaleiro, J. Chem. Soc., Chem. Comm., (1992) 855.

[20] S.K. Chang, H.S. Hwang, H. Son, J. Youk and Y.S. Kang, J. Chem. Soc., Chem. Comm., (1991) 217.

[21] K. Odashima, K. Yagi, K. Tohda and Y. Umezawa, Anal. Chem., 65 (1993) 1074.

[22] W.H. Chan, K.K. Shiu and X.H. Gu, Analyst, 118 (1993) 863.

[23] C.D. Gutsche, J.A. Levine, J. Am. Chem. Soc., 104 (1982) 2652.

[24] C.D. Gutsche, J.A. Levine, P.K. Sujeeth, J. Org. Chem., 50 (1985) 5802.

[25] F. Arnaud-Neu, M.J. Schwing-Weill, K. Ziat, S. Cremin, S.J. Harris and M.A. McKervey, New J. Chem., 15 (1991) 33–37.

[26] H. Small, in D. Hercules (Editor), Ion Chromatography, Modern Analytical Chemistry Series, Plenum Press, New York, 1989.