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CHROMATOGRAPHIC SEPARATIONS OF ALKALI AND ALKALINE EARTH METAL CATIONS AND SOME ANIONS ON BENZO-18-CROWN-6-MODIFIED SILICAS

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SUMMARY

The chromatographic behaviour of alkali and alkaline earth metal halides on benzo-18-crown-6-modified silicas was investigated with water as the mobile phase. Very good separations were obtained for the two series, except for the pair $\text{Ca}^{2+}/\text{Mg}^{2+}$, in less than 30 min. Separations of mixtures of alkali and alkaline earth metal cations were also observed. Moreover, a very efficient separation of the anions Cl^- , Br^- , I^- , NO_3^- and SCN^- was observed, partly as a result of the hydrophobic character of the exchanger. This illustrates the exceptional binding properties of crown ethers and offers new possibilities in liquid chromatography.

INTRODUCTION

Research on crown ethers and cryptands has developed rapidly since the discovery of their binding properties for various metal ions. The use of these ligands in analytical chemistry¹ and in catalysis² has received considerable attention, mainly because of their unique properties of forming complexes with alkali and alkaline earth metal cations. These ligands have been employed as reagents in liquid chromatography. In 1974, Blasius *et al.*³ published the first paper describing the separation of cations with an ion exchanger having such ligands covalently bonded to it. The work carried out on this subject was recently reviewed by Kimura and Shono⁴. These studies showed that the quality of the separations depends strongly on the chemical structure of the bonded crown ether or cryptand and on the method of preparation of the exchanger.

Among the supports used for the immobilization of the crown ethers, inorganic materials such as silica seem to be preferable when pressure is required in liquid chromatography. Recently we reported⁵ preliminary results on the synthesis, binding properties and separation properties of a silica phase grafted with benzo-18-crown-6. In a previous paper⁶, we described different methods of preparing four benzo-18-crown-6-grafted silicas, discussed the advantages of each method and compared their binding properties at equilibrium. In this paper, we report the separation of alkali and alkaline earth metal ions, mixtures of alkali and alkaline earth metal halides and anions.

EXPERIMENTAL

The synthesis and binding properties of the two grafted silicas used have been described previously⁶.

The silicas slurried in carbon tetrachloride were packed into a stainless-steel column (13 cm × 0.48 cm I.D.) under 300 bar pressure.

The chromatographic experiments were performed with a chromatographic system assembled from commercially available modules consisting of a pump with a pressure indicator (Milton Roy Imp 70), a sample injector (Chromatem 70-10), a conductivity detector (Taccusel CD-6-N) and a recorder (Philips PM 8100). Aliquots of 20 μ l of 0.1 M aqueous mixed salt solutions were injected. The flow-rate ranged from 0.16 to 0.26 ml/min. Water served as the mobile phase.

RESULTS AND DISCUSSION

Silica particles of 10 μ m (Silica 10) and 30 μ m (Silica 30) diameter were modified by bonding benzo-18-crown-6 to their surfaces (Fig. 1). Both column materials had approximately the same concentration of crown ether (0.2 mmol/g) according to the results of carbon analyses. Silica 30 columns equilibrated in 10 min whereas Silica 10 columns required 15 min. The difference in equilibration times might be due to differences in pore size.

Separation of alkali metal halides

The separation of alkali metal chlorides using Silica 10 and 30 stationary phases with water as the mobile phase is illustrated in Fig. 2. Lithium, sodium, potassium, rubidium and caesium chlorides were completely separated in 30 min. Except for caesium chloride, the elution order agrees with the estimated stability constants for alkali metal-benzo-18-crown-6 complexes in aqueous systems (Table 1). The long retention time of caesium chloride, which is unexpected on the basis of the stability constant for Cs-benzo-18-crown-6, might be caused by the formation of a "sandwich" complex $[\text{Cs}(\text{benzo-18-crown-6})_2]^+$. Such sandwich complexes are often observed when the diameter of the cation is greater than the cavity size of the macrocycle⁷. Although such a complex has not yet been described for caesium and benzo-18-crown-6, the substantial local concentration of ligands on silica should favour its formation.

The characteristic chromatographic parameters for these separations are summarized in Table I. The values for k' , N and α clearly indicate that these column materials are well suited for the separation of alkali metal ions. The values of R_s are equal to or larger than 0.8, a value characteristic of good resolution. When alkali

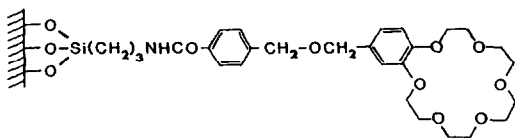


Fig. 1. Structure of benzo-18-crown-6-modified silica.

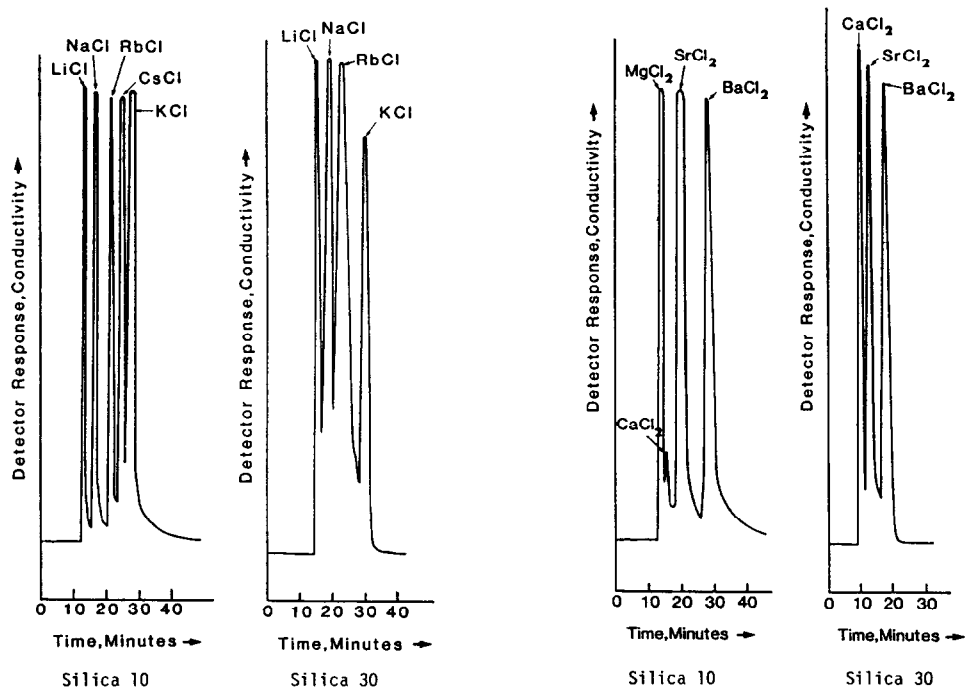


Fig. 2. Separation of alkali metal chlorides on benzo-18-crown-6-modified silica.

Fig. 3. Separation of alkaline earth metal chlorides on benzo-18-crown-6-modified silica.

TABLE I

SEPARATION OF ALKALI METAL CHLORIDES ON BENZO-18-CROWN-6-MODIFIED SILICAS

Parameter	Silica 10					Silica 30			
	LiCl	NaCl	RbCl	CsCl	KCl	LiCl	NaCl	RbCl	KCl
Amount injected (μg)	25	35	48	67	112	42	58	121	75
Retention time, t_R (min)	12	15	20	23.5	26	15	18	22.5	30
Capacity factor, k' ^{***}	0	0.3	0.7	1.0	1.2	0	0.2	0.2	1.0
Stability constant, $\text{p}K_E$	—	1.0*	1.4*	0.8*	1.8**	—	1.0*	1.4*	1.8**
Theoretical plates, N [§]	910	850	1020	1380	590	900	260	140	1075
Selectivity, α ^{§§}	—	—	2.7	1.4	1.2	—	—	2.5	2.0
Resolution, R_s ^{§§§}	—	1.7	2.2	1.3	0.8	—	1.0	0.8	1.3

* Values estimated from data in ref. 8.

** Ref. 5.

*** $k' = (t_R - t_0)/t_0$.§ $N = 5.54(t_R/\delta)^2$ where δ = peak width at half-height.§§ $\alpha = k'_1/k'_2$.§§§ $R_s = 2(t_{R1} - t_{R2})/(W_1 + W_2)$, where W = peak width at base.

TABLE II

SEPARATION OF ALKALINE EARTH METAL CHLORIDES ON BENZO-18-CROWN-6-MODIFIED SILICAS

Parameter	Silica 10				Silica 30		
	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂	CaCl ₂	SrCl ₂	BaCl ₂
Amount injected (μg)	29	11	95	208	56	79	104
Retention time, <i>t_R</i> (min)	13.5	15	19	28	10	12.5	17.5
Capacity factor, <i>k'</i>	0.1	0.3	0.6	1.3	0.1	0.4	0.9
Stability constant, p <i>K_E</i>	—	< 0.5*	1.9**	2.7**	< 0.5*	1.9**	2.7**
Theoretical plates, <i>N</i>	400	—	275	595	400	280	545
Selectivity, α	—	2.0	2.3	2.3	—	3.5	2.4
Resolution, <i>R_s</i>	—	< 0.6	1.1	1.9	—	1.0	1.7

* Values estimated from data in ref. 8.

** Ref. 5.

metal bromides or thiocyanates were chromatographed under these conditions, the separations were marginally better.

Separation of alkaline earth metal chlorides

Chromatograms of alkaline earth metal chlorides obtained with Silica 10 and 30 are shown in Fig. 3. The alkaline earth metal ions elute in the sequence Mg²⁺ < Ca²⁺ < Sr²⁺ < Ba²⁺, in accordance with the values of p*K_E* (Table II). Only Mg²⁺ and Ca²⁺ were poorly separated.

With poly(benzo-15-crown-5)-modified silica, Nakajima *et al.*⁹ achieved such a separation only with water-methanol (50:50) as the mobile phase. The capacity factors (*k'*) for alkaline earth metal cations are much lower than those for alkali metal cations, although the values of p*K_E* are comparable. This effect can be partly attributed to the hydrophobic character of the modified silicas, which partly excludes the more hydrated alkaline earth metal cations.

Comparison of the number of theoretical plates obtained with Silica 30 and Silica 10 clearly indicates that the best results were obtained with the finer phase.

Separation of mixtures of alkali and alkaline earth metal chlorides

Mixtures of alkali and alkaline earth metal salts can be separated with classical ion-exchange resins only by using gradient elution. Such separations are possible with water as the mobile phase when crown ether-grafted silicas are used as column materials (Fig. 4). The good separations obtained with selected cations in order to avoid overlapping (Table III) illustrate the possibilities of such phases.

Separations of anions

We have already observed that the capacities of these silicas for cations depend strongly on the type of anion⁶. For example, the capacities obtained with thiocyanate (a lipophilic anion) are about twice those obtained with chloride. Again, this is clearly understood by considering the hydrophobic character of these stationary phases. The

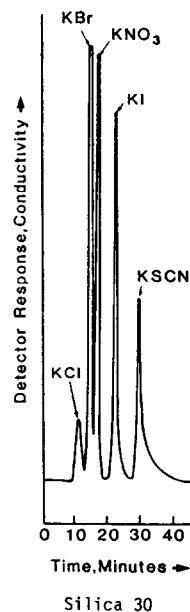
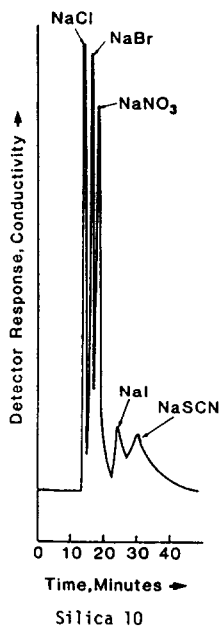
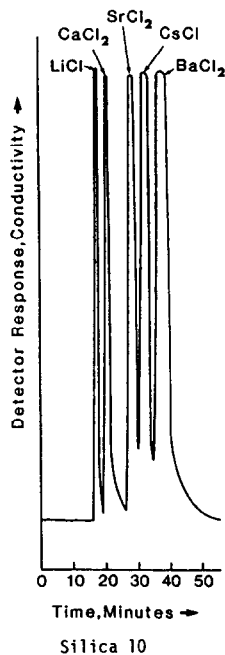


Fig. 4. Separation of a mixture of alkali and alkaline earth metal chlorides on benzo-18-crown-6-modified silica.

Fig. 5. Separation of anions on benzo-18-crown-6-modified silica.

separations of chloride, bromide, nitrate, iodide and thiocyanate of potassium and sodium (Table IV) are shown in Fig. 5. Very good separations were obtained without difficulty and, as expected, the characteristics of the separation were improved by using a cation that has a large affinity for the stationary phase (*e.g.*, potassium).

TABLE III

SEPARATION OF A MIXTURE OF ALKALI AND ALKALINE EARTH METAL CHLORIDES ON SILICA 10

Parameter	LiCl	CaCl ₂	SrCl ₂	CsCl	BaCl ₂
Amount injected (μg)	21	33	48	84	208
Retention time, t_R (min)	16.5	19.5	27.5	31.5	37
Capacity factor, k'	0	0.2	0.7	0.9	1.2
Stability constant, $\text{p}K_E$	—	< 0.5*	1.9**	0.8*	2.7**
Theoretical plates, N	1030	810	535	755	410
Selectivity, α	—	—	3.7	1.4	1.4
Resolution, R_s	—	1.2	2.1	0.9	1.0

* Ref. 8.

** Ref. 5.

TABLE IV
CHROMATOGRAPHIC SEPARATION OF ANIONS

Parameter	Silica 10					Silica 30				
	NaCl	NaBr	NaNO ₃	NaI	NaSCN	KCl	KBr	KNO ₃	KI	KSCN
Amount injected (μg)	18	41	43	120	162	30	48	40	100	117
Retention time, t_R (min)	13.5	15.5	17.5	23.5	29	11	14	16	21.5	28.5
Capacity factor, k'	0.2	0.3	0.5	1.0	1.5	0.2	0.6	0.8	1.4	2.2
Theoretical plates, N	1300	960	780	180	110	145	740	1220	460	360
Selectivity, α		2.0	1.5	2.0	1.5		2.5	1.4	1.8	1.6
Resolution, R_s		1.1	0.9	1.3	0.6		1.0	1.0	1.8	1.4

CONCLUSION

The results of the separations of alkali metal cations, alkaline earth metal cations, cation mixtures and anions illustrate the exceptional binding properties of crown ethers. It is believed that such exchangers offer new and simple separation possibilities. Good separations can be obtained with water as the mobile phase. Non-aqueous eluents, gradient elution or acid or basic eluents that require the use of a neutralization column are not needed. However, the applicability of this method to "real" samples necessitates further work. In particular, the presence of different anions in the samples may result in difficulties of identification. Possibilities exist and work is in progress in this direction.

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