Ion Chromatographic Retention Mechanism of Inorganic Anions on Macrocycle Based Stationary Phase

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Abstract

Retention behaviour of inorganic anions was investigated on a cryptand-based anion exchange column (Cryptand A1) using NaOH and KOH-based eluents. Due to the ability of the macrocycle to bind cations, the positively charged metal-cryptand complexes act as anion exchange sites. In addition, cryptand can be partially protonated and in this form also behaves as anion exchanger. Considering the complexation and protonation mechanisms a theoretical retention model and a general equation were developed for describing the simultaneous effect of the nature and concentration of the eluent on the retention factor k. The parameters of the model were iterated and the ion exchange constants were computed, theoretical and experimental data show a good correspondence with correlation coefficients (r^2) 0.9987-0.9998 for KOH and 0.9717-0.9883 for NaOH, experimental and computed data differ maximally 5%.

Keywords: ion chromatography, retention mechanism, macrocyclic ligand.

1. Introduction

Since the macrocyclic polyethers were discovered in 1967 they have been noted for their unique complexing abilities. Their capability to selectively complex cations has opened the door to several broad and fruitful areas of chemical investigation. Column liquid chromatographic applications of macrocyclic ligands have focused on primarily ion separations,[1–9] although other species have also been separated.[10–12]

The selectivity of macrocycles for cations is determined by the ability of the cation to fit into the central cavity of the macrocycle and by the desolvation energy of the cation. The thermodynamic stabilites of the cryptate complexes strongly depend on the match of the cation size and cryptand cavity diameters. For example equilibrium constants ($\log K$) for complexation of alkali metal cations with 2.2.2-cryptand (r = 1.4 Å) are: Li$^+$ (r = 0.68 Å) 1.25; Na$^+$ (r = 0.95 Å) 3.9; K$^+$ (r = 1.33 Å) 5.4; Rb$^+$ (r = 1.48 Å) 4.35; Cs$^+$ (r = 1.69 Å) < 2.[13] The protonation and binding constants of metal ions in aqueous solution with the parent compounds of these ligands have been tabulated.[14–16]

Anions, contrary to cations, can be separated on a macrocycle column through ion-exchange mechanism rather than ligand-exchange mechanism. Since most macrocycles are neutral molecules, when the cations are complexed into the macrocycle, a positively charged functional group is generated, which then provides the site for anion exchange. Sample anions can be eluted using alkali metal hydroxide eluent. The alkali metal cation with the macrocycle forms the positively charged anion exchange sites, while the hydroxide ion serves to elute the anion. The ion exchange capacity of the column depends on the binding constant of the complexed cation. A greater binding constant of the metal ion to the macrocycle means greater capacity of the column at a given eluent concentration. Although crown ethers have found use in cation separations, they have found only limited use as anion exchangers. Cryptands, due to their stronger ability to bind certain cations, were found to be quite suitable in anion-exchange separations.

During anion separation the capacity of the column can be adjusted by the choice of the type and the concentration of the eluent cation. The greatest advantage of cryptand-based column is the possibility to perform the so

called "capacity gradient"[17] during elution. Gradient elution in ion chromatography generally causes baseline distortion which can interfere in the detection of sample anions. By changing the capacity of the column instead of the eluent strength the efficiency of the separation can be increased keeping a stable baseline. The capacity gradient can be performed by five ways: (1) changing the eluent cation, but keeping the eluent concentration constant,[1,4,5,8,18–20] (2) changing the eluent to water,[11,19] (3) using cation gradient,[10] (4) changing the temperature,[3,4,8] or (5) changing the organic solvent content[8] of the mobile phase.

Although there is a lot of work in the field of anion separation on macrocycle based anion-exchange chromatography, there is no modelling of the retention considering all the proceeding mechanisms.
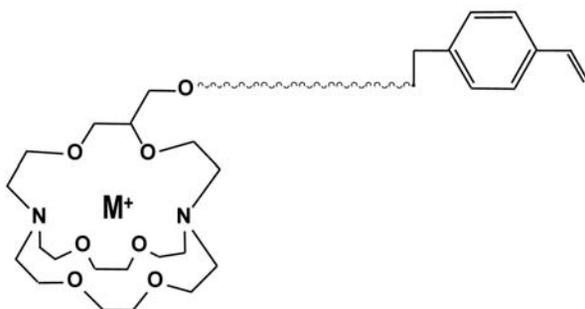
Figure 1. Structure of the *n*-decyl-2.2.2 cryptand present in the Cryptand A1 column.

In our work we report a systematic investigation on a cryptand-based anion exchange column containing covalently bound *n*-decyl-2.2.2 cryptand (D222) (Figure 1)[18–20] by separation of five common anions using NaOH and KOH eluent and suppressed conductivity detection.

We also describe a retention mechanism for the sample anions considering the complexation of the cryptand with alkali cation, protonation of the bridge nitrogen atoms and the ion exchange on these anion-exchanger sites.

2. Experimental

2.1 Materials

All chemicals used for eluent and sample preparation were reagent grade. The NaOH and KOH for eluents were from Merck (Darmstadt, Germany). Concentrations of eluents were: 0.0005, 0.001, 0.002, 0.003, 0.004, 0.005, 0.007, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1 M NaOH, and 0.001, 0.003, 0.005, 0.007, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04, 0.06, 0.08, 0.1 M KOH. Sample solutions such as 3 mg L^{-1} Cl^-, 5 mg L^{-1} NO_2^-, 10 mg L^{-1} NO_3^-, 5 mg L^{-1} Br^-, 3 mg L^{-1} BrO_3^- were diluted from 1000 mg L^{-1} of stock solution of each component. Puri-

fied water (18.2 MΩ resistivity) used for eluent and sample preparation was obtained with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Eluents were daily prepared and filtered through 0.22 μm filters (Millipore).

2.2 Instrumentation

A DX 500 (Dionex, Sunnyvale, CA, USA) microbore ion chromatograph consisting of a quaternary gradient pump (GP40) and suppressed conductivity detection (Dionex ED50) was used for all analyses. A post-column eluent conductivity suppression was achieved using an Anion Self-Regenerating Suppressor (Dionex ASRS-Ultra, 2 mm) in the internal water mode. The background conductivity of the suppressed eluent was approximately 1.2 μS. The analytical column was an IonPac Cryptand A1 5 μm (150 mm × 3 mm i.d.) from Dionex (column capacity 73 μeq). Eluent flow rate was 0.5 mL min^{-1}. The dead volume of the system containing Cryptand A1 column was 0.685 ml and without the column it was 0.110 mL. However, it has also been noted that the former changed negligibly (±1%) during investigations. The volume of the sample loop was 25 μL. To remove carbonate from the eluents, an Ion-Pac ATC 2 mm trap column was inserted in-line between the pump and the injector in place of the High Pressure Gradient Mixer. Instrument control and data collection were performed with the Chromeleon Workstation (Dionex). Data processing was performed by using PeakNet 6.0 (Dionex) and Excel XP version (Microsoft Corp.).

2.3. Multi-Variable Regression

Calculation and graphic elaborations were performed using an IBM-compatible PC with the Mathematica 5.1 (Wolfram Research Inc.). The multi-variable non-linear regression analysis was realized by fitting the retention data to the derived model with the named variables and parameters, returning a list of rules expressing the fit parameter estimates. The estimates of the model parameters are chosen to minimize the χ^2 merit function given by the sum of squared residuals. The optimization method used was iterative so starting values were required for the parameter estimate search. Careful choice of starting values was necessary, as the parameter estimates found may represent a local minimum in the χ^2 merit function. The Levenberg-Marquardt method was used during the calculations, which gradually shifts the search for the minimum of χ^2 from steepest descent to quadratic minimization.

3. Theory

The Cryptand A1 column uses lithium, sodium or potassium hydroxide eluents with each eluent producing a different column capacity range. The capacity of the co-

lumn is related to the binding constant of the complexed cation for the cryptand functional group. The process of cation-macrocycle association depends on several factors related to characteristic properties of the ligand, reacting cation, and solvent.

Since the stationary phase macrocycles contain nitrogen bridge atoms in the ring, they can be protonated under the proper conditions. This is an additional way in which positively charged anion exchange sites may be generated. The $\log K$ values for nitrogens of 2.2.2 cryptand molecule are 10.0 and 7.5.[7] Considering that these protonation constants were determined for 2.2.2 cryptand in water, not for *n*-decyl-2.2.2 cryptand grafted on styrene-divinylbenzene resin (Cryptand A1), these coefficients were just starting values, the correct values have to be determined on the basis of the measured database. However, assumed that the first and second protonation coefficients of covalently bound D222 are close to 10.0 and 7.5, it can be predicted that the stationary phase is partially protonated in the used experimental conditions ($c_{OH^-} = 0.001–0.1$ mol L^{-1}). Thus the reactions that can take place in the column to form anion exchange sites are protonation of each macrocyclic nitrogens and binding of the metal ion.

3.1. Complexation and Protonation Equilibria

Cryptand stationary phase, as mentioned, is able to coordinate metal ions and, since the macrocycle contains nitrogen atoms in the ring, can also be protonated at the proper pH values. For the elution of aqueous solution of an alkali cation the equilibria involved and their constants are:

$$Cy + M^+ \overset{K_M}{\Leftrightarrow} CyM^+, \tag{1}$$

$$Cy + H^+ \overset{K_1}{\Leftrightarrow} CyH^+, \tag{2}$$

$$CyH^+ + H^+ \overset{K_2}{\Leftrightarrow} CyH_2^{2+}, \tag{3}$$
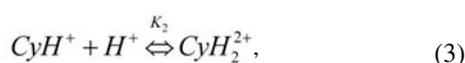
$$K_M = \frac{(CyM^+)}{(Cy)[M^+]}, \tag{4}$$

$$K_1 = \frac{(CyH^+)}{(Cy)[H^+]}, \tag{5}$$

$$K_2 = \frac{(CyH_2^{2+})}{(CyH^+)[H^+]}, \tag{6}$$

where (Cy) are the free sites on the stationary phase and M$^+$ the eluent cations, and the round and square brackets refer to the stationary and mobile phases, respectively.

3.2. Ion-Exchange Equilibria

Any positively charged site on cryptand could be assumed as an ion-exchange site but, considering the protonation constants (pK_a) of the nitrogens within the macrocycle ($\log K_1$ 10, $\log K_2$ 7.5) under the working conditions only CyH$^+$ and CyM$^+$ can be considered active sites characterised, in the presence of an aqueous eluent (e.g. NaOH), by their counter ion, OH$^-$. The ion exchange equilibria and the respective constants involved (selectivity coefficients, $K_{A/OH}$), in the retention mechanism of a negatively charged analyte, A$^-$, will be:

$$CyM^+ + OH^- \overset{K_{M-OH}}{\Leftrightarrow} CyMOH, \tag{7}$$

$$CyM^+ + A^- \overset{K_{M-A}}{\Leftrightarrow} CyMA, \tag{8}$$

$$CyH^+ + OH^- \overset{K_{H-OH}}{\Leftrightarrow} CyHOH \Rightarrow Cy + H_2O, \tag{9}$$

$$CyH^+ + A^- \overset{K_{H-A}}{\Leftrightarrow} CyHA, \tag{10}$$

$$K_{M-OH} = \frac{(CyMOH)}{(CyM^+)[OH^-]}, \tag{11}$$

$$K_{M-A} = \frac{(CyMA)}{(CyM^+)[A^-]}, \tag{12}$$

$$K_{H-OH} = \frac{(Cy)}{(CyH^+)[OH^-]} = \frac{1}{K_1 K_w}, \tag{13}$$

$$K_{H-A} = \frac{(CyHA)}{(CyH^+)[A^-]}. \tag{14}$$

Maximal ion-exchange capacity (in other words, the saturation capacity = 0.152 meq mL^{-1}) of the column will be:

$$Q = Cy_T = (Cy) + (CyM^+) + (CyH^+) + \\ + (CyMOH) + (CyMA) + (CyHA), \tag{15}$$

where Cy$_T$ are the total sites of the column and (CyH$_2^{2+}$) has been omitted since at the working pH values this species is not originated.

Now, by deriving (CyM$^+$), (CyH$^+$), (CyMOH), (CyMA) and (CyHA) from Eqs. (4), (5), (11), (12) and (14) as follows:

$$(CyM^+) = K_M (Cy) [M^+], \tag{16}$$

$$(CyH^+) = K_1 (Cy) [H^+], \tag{17}$$

$$(CyMOH) = K_{M-OH} (CyM^+)[OH^-] = \\ = K_{M-OH} K_M (Cy) [M^+][OH^-], \tag{18}$$

$(CyMA) = K_{M-A} (CyM^+) [A^-] =$

$= K_{M-A} K_M (Cy) [M^+][A^-] ,$ (19)

$(CyHA) = K_{H-A} (CyH^+) [A^-] =$

$= K_{H-A} K_1 (Cy) [H^+] [A^-] ,$ (20)

we can write:

$Q = CyT = (Cy) (1+ K_M[M^+] + K_1[H^+] +$

$+ K_{M-OH} K_M [M^+][OH^-] + K_{M-A} K_M [M^+][A^-] +$

$+ K_{H-A} K_1 [H^+][A^-]) .$

Keeping in mind now the distribution coefficient for the analyte anion:

$$D_A = \frac{(A^-)}{[A^-]} = \frac{(CyMA)+(CyHA)}{[A^-]} ,$$ (21)

we obtain:

$$D_A = Q \frac{[M^+] K_M K_{M-A}+[H^+] K_1 K_{H-A}}{1+[H^+] K_1 \left(1+[A^-] K_{H-A}\right)+[M^+] K_M \left(1+[A^-] K_{M-A}+[OH^-] K_{M-OH}\right)} .$$ (22)

Almost all analytical applications of chromatography are carried out under linear conditions, i.e. in the linear range of the equilibrium isotherm where the equilibrium concentrations of the solute in the stationary and the mobile phases are directly proportional due to the small concentration of the analyte. As a consequence, the terms $[A^-] + \underline{K}_{H-A}$ and $[A^-] + K_{H-A}$ can be neglected from Eq. (22) which simplifies into the following form:

$$D_A = Q \frac{[M^+] K_M K_{M-A}+[H^+] K_1 K_{H-A}}{1+[H^+] K_1+[M^+] K_M \left(1+[OH^-] K_{M-OH}\right)} ,$$ (23)

where, due to the eluent composition, $[M^+] = [OH^-]$ and, as previously defined, $Q = (C_{yT}) = 0.152$ meq mL^{-1}.

3.3 Calculations

Distribution coefficients can be calculated by using the measured retention factor *k* as follows:

$$D_{A/OH} = \frac{V_s}{V_0} k ,$$

where V_s is the volume of the stationary phase and V_0 is the volume of the mobile phase. Retention factors were evaluated for a relatively wide range of eluent concentrations (NaOH: 0.0005 – 0.1 mol L^{-1}, KOH: 0.001 – 0.1 mol L^{-1}).

On the basis of these calculated distribution coefficients from the retention database the unknown parameters of Eq. (23) were iterated and simultaneously, curves were fitted to the measured data points using the above mentioned multivariate regression. As above mentioned, during the iteration process the second protonation equilibrium was neglected. For NaOH eluent as a first step of the iteration process, the protonation constant of the cryptand molecule was kept constant ($\log K_1 = 10$)[7] and the remaining parameters (K_M, K_{M-A}, K_{HA}, K_{M-OH}) were iterated. The binding constant of the sodium ion was calculated as an averaged value from the results of the first iteration step. In the second step, three parameters of Eq. (23), namely K_{M-A}, K_{HA} and K_{M-OH} were reiterated keeping constant both the protonation and the binding constants previously obtained. In the third step the experimental protonation constant was re-evaluated by iteration introducing the values of parameters calculated in the second step. For KOH eluent, assuming the ratio of thermodynamic binding constants ($K_K/K_{Na} = 31.6$),[13] K_K was calculated from the K_{Na} previously obtained and kept constant as well as the protonation and K_{HA} constants. K_{M-A} and K_{M-OH} parameters were computed.

4 Results and Discussion

4.1 Effect of Eluent Type and Concentration on the Retention of Inorganic Anions

The effect of NaOH and KOH on the retention factors for the investigated inorganic anions is shown in Figures 2 and 3 (symbols), respectively.
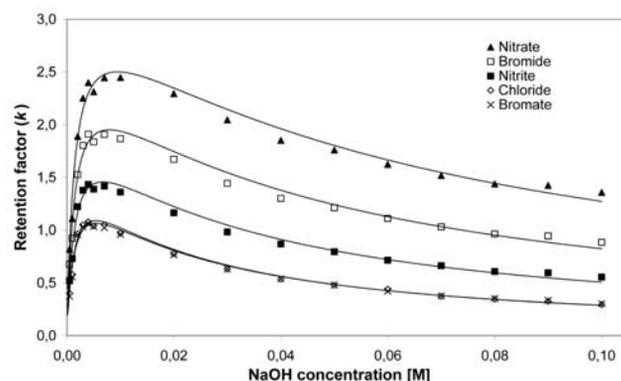
Figure 2. Effect of NaOH concentration on the retention factors (symbols); *k* predicted by Eq.23 for all the analytes studied (solid line). Column: Cryptand A1 5 μm (150 mm × 3 mm i.d.). Eluent: NaOH as shown. Eluent flow rate: 0.5 mL min^{-1}.
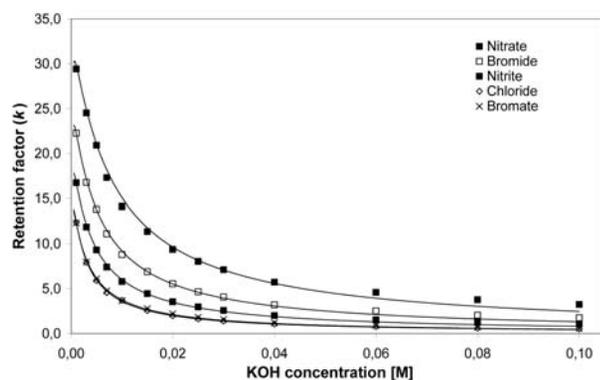
Figure 3. Effect of KOH concentration on the retention factors (symbols); *k* predicted by Eq.23 for all the analytes studied (solid line). Column: Cryptand A1 5 µm (150 mm × 3 mm i.d.). Eluent: KOH as shown. Eluent flow rate: 0.5 mL min^{-1}.

It can be seen (Figure 2) that *k* data, for NaOH eluent, increase with the eluent concentration reaching a maximum at 0.004 mol L^{-1}, following which they decrease. This behaviour could be ascribed to two simultaneous and competitive mechanisms: (i) the increase of the column capacity, (ii) the competition for the anion exchange sites between analytes and eluent counter anion as the eluent concentration is increasing. This means that at lower NaOH concentrations the predominant mechanism is the increase of the capacity and beyond 0.004 mol L^{-1} NaOH the predominant effect is the competition. For the KOH eluent retention factors follow a decreasing profile showing that at the lower KOH concentration investigated the maximum capacity of the column is already reached. This could be explained considering the thermodynamic binding constants to the cryptand for NaOH and KOH.[13] By comparing the retention data for inorganic anions it can be observed that using KOH the retention factors are much greater than in the case of NaOH at the same ion strength and pH but the selectivity is the same following the order of traditional strong ion exchangers.
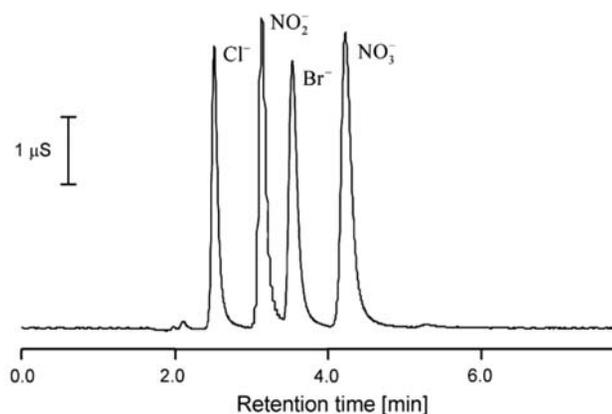
Figure 4. Typical chromatogram for elution of analytes. Column: Cryptand A1 5 µm (150 mm × 3 mm i.d.). Eluent: 0.01 M NaOH. Sample loop: 25 µL. Analyte concentrations: 3 mg L^{-1} Cl$^-$, 5 mg L^{-1} NO$_2^-$, 5 mg L^{-1} Br$^-$, 10 mg L^{-1} NO$_3^-$. Eluent flow rate: 0.5 mL min^{-1}.

Figure 4 shows a typical chromatogram obtained throughout this work where the presence of BrO$_3^-$ has been omitted due to its coelution with Cl$^-$ peak as depicted in Figures 2 and 3. It should be remarked that at this stage, the aim of the paper is the modelling of analyte retention and not optimisation of their separation.

4.2 Calculated Constants

Table 1. Values of the computed *K*.

Constant	BrO$_3^-$	Cl$^-$	NO$_2^-$	Br$^-$	NO$_3^-$
K_1		1.1×10^{10} (RSD%=2.4%)			
K_{Na}		755 (RSD%=4.8%)			
K_K		23,860			
K_{Na-A}	12.5	12.9	16.1	20.6	25.3
K_{K-A}	137	142	173	219	274
K_{H-A}	3.6	2.2	1.9	2.6	5.2
K_{Na-OH}	45	47	30	22	15
K_{K-OH}	362	400	265	201	132

Where: K_1 protonation constant; K_{Na} and K_K binding constants of Na$^+$ and K$^+$ to the cryptand, K_{Na-A} and K_{K-A} exchange constant of A$^-$ to the metal-cryptand complex, K_{H-A} exchange constant of A$^-$ on the protonated cryptand, K_{Na-OH} and K_{K-OH} adsorption constant of OH$^-$ on the metal-cryptand complex.

It can be seen that the protonation constant K$_1$ remained close to the literature value (RSD% = 2.4%), however, the binding constants of Na$^+$ and K$^+$ to the cryptand are smaller than the literature values for homogeneous systems (RSD% = 4.8%). The magnitude of the adsorption constants (K_{NaA}, K_{KA}) is related, of course, to the chromatographic behaviour of anions and their retention order follows the trend of the constant values. By comparing these adsorption constants it can be underlined that the difference between them is about one order of magnitude indicating higher affinity of analytes for potassium sites which are acting in a similar way as a strong anion exchanger.[21] As expected, the values of K_{HA} are low and they confirm the reduced contribution to the whole retention mechanism especially in the case of cryptand-K system. The behaviour and values for K_{MOH} seem slightly dependant on the analyte nature and follow the reverse order of K_{MA}, this situation could be supported by the influence of foreign ions on the interaction with the cryptand as shown in organic systems[22]. This behaviour is also supported by the ion-exchange selectivity of traditional anion-exchangers, which explains the greater affinity of analytes for the fixed sites of the stationary phase respect to the hydroxide ion. Figures 2 and 3 (see above) also compare experimental and computed data of *k* for each anion and for both NaOH and KOH eluents, respectively, where, as underlined also by Table 2, a good correspondence is shown.

The low Δ_{mean} values (average for each eluent composition of $\Delta = 100 \cdot \frac{k_{exp} - k_{calc}}{k_{exp}}$), together with the RSD and r^2 values confirm the validity of the model proposed.

Table 2. Correlation coefficients and relative standard deviations for the experimental and computed values.

		BrO_3^-	Cl^-	NO_2^-	Br^-	NO_3^-
NaOH	Δ_{mean} (%)	1.6	1.4	1.9	2.1	2.1
n=17	RSD	0.82	0.71	0.62	0.75	1.0
	Intersect.	0.021	–0.002	–0.039	–0.009	0.126
	slope	0.990	1.000	1.014	1.002	0.964
	r^2	0.9830	0.9883	0.9814	0.9765	0.9717
KOH	Δ_{mean} (%)	3.5	1.8	4.1	4.6	5.0
n=13	RSD	0.73	0.83	0.97	1.1	1.3
	Intersect.	–0.149	–0.066	–0.223	–0.322	–0.533
	slope	1.016	1.007	1.017	1.019	1.023
	r^2	0.9996	0.9998	0.9989	0.9987	0.9988

Where $\Delta(\%) = 100 \cdot \dfrac{k_{exp} - k_{calc}}{k_{exp}}$ and Δ_{mean} (%) are averaged for all the eluents compositions evaluated.

5. Conclusions

A theoretical retention model has been developed for a cryptand based anion exchange column where an unconventional mechanism is involved. The simultaneous effect of nature and concentration of eluent cation on the chromatographic behaviour for five inorganic anions have been evaluated and through a general equation protonation, binding and exchange constants have been calculated. A satisfactory correlation between computed and experimental values has been obtained, within error not higher than 5%, supporting the developed model.

6. Acknowledgements

7. References

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Povzetek

Preučevali smo retencijo anorganskih anionov na anionski izmenjalni koloni na osnovi kriptanda (Cryptand A1) z uporabo eluentov na osnovi NaOH in KOH. Zaradi zmožnosti makrocikličnih spojin, da vežejo katione, se kompleksi kovina-kriptand, ki so pozitivno nabiti, obnašajo kot anionsko izmenjalna mesta. Poleg tega se lahko kriptand delno protonira in deluje kot anionski izmenjalec. Oziraje se na procese kompleksiranja in protonacije smo razvili teoretični retencijski model in splošno enačbo, ki opisuje hkratni vpliv vrste in koncentracije eluenta na retencijski koeficient *k*. Z iteracijo parametrov modela smo izračunali konstante za ionsko izmenjavo, pri čemer so teoretični in eksperimentalni podatki dobro primerljivi, s korelacijskimi koeficienti (r^2) 0,9987 – 0,9998 za KOH in 0,9717 – 0,9883 za NaOH, pri čemer se eksperimentalni in izračunani podatki razlikujejo največ za 5 %.