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Potassium Selective Acrylic Resins: Synthesis and Application to Chemical Sensors

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Abstract

Crosslinked copolymers based on poly(acrylic acid) and functionalised with crown ethers have been designed and synthesised. The materials selectively absorb K^+ over other Group I ions such as Li^+ and Na^+ . The copolymers have been used as the basis of a quartz crystal microbalance, QCM, to form a sensor for aqueous solutions. Acrylic acid polymers cross-linked with ethylene-glycol-dimethacrylate, (EGDMA) and substituted with 18-crown-6 and the 15-crown-5 rings were coated onto the crystal and the sensing of $K^+_{(aq)}$ investigated. The detection limit of the developed sensor is estimated at 0.1- 0.2 ppm for $K^+_{(aq)}$ with a linear range extending to over 1000 ppm although further optimisation should significantly improve this performance.

Keywords: Quartz Crystal Microbalance; chemical sensor; acrylic acid copolymer; crown ether polymers; functional monomer.

1. Introduction

The ability to synthesise polymers with closely defined structure and properties has been one of the major advances in materials chemistry over the past two decades [1]. It is now possible to tailor polymers and copolymers with precisely distributed functional groups which can respond to external stimuli or conditions. Examples of application include controlled delivery systems, photo- and thermally responsive materials and as specific absorbents. Our interest lies in the last of these areas where functionalized polymers are used to provide the species selectivity for chemical sensors.

The development of new chemical sensors is an active area of research [2]. There are two essential components of a sensor system; detection and transduction or reporting. The first of these relies on some specific chemical interaction between the analyte of interest and a component of the sensor. The second, produces a measurable signal which reports that the interaction is taking place. The transducer system influences the type of interaction that can be monitored; for example optical transduction requires a change in absorption or emission properties of the analyte. We have been working with piezoelectric transduction [3] where the property of interest is the oscillation frequency of a crystal, typically quartz. The frequency, F , is influenced by the mass and/or viscoelasticity of any coating on the crystal.

A piezoelectric device, known as a quartz crystal microbalance, QCM, is well established in thin-film monitoring [4]. For a crystal oscillating at 10 MHz, the theoretical detection limit [5] is around 1×10^{-12} g so that it is potentially a very sensitive mass detector. Values close to this have been achieved when used in the gas phase although the sensitivity is lowered in solution but can nonetheless measure sub-nanogram mass changes under optimum conditions. However, the surface of the resonator, which is usually a thin gold coating, is non specific and so has little specificity as a sensor.

The surface of a resonator can be modified with a film to selectively bind a particular

species. The majority of QCM sensors reported are designed to operate in the gas phase, for example organic vapour detection. Operation in solution is more difficult due to the damping of the liquid. However, these problems can be overcome by design of suitable electronics and sensor systems have been developed where only one face of the crystal is exposed to the viscous fluid. In addition to sensors, such systems have been used to study biological recognition [6] and electrochemical systems. Polymer based systems have been used in aqueous QCM sensors including calixarenes, crown-ethers and molecularly imprinted polymers [7-9].

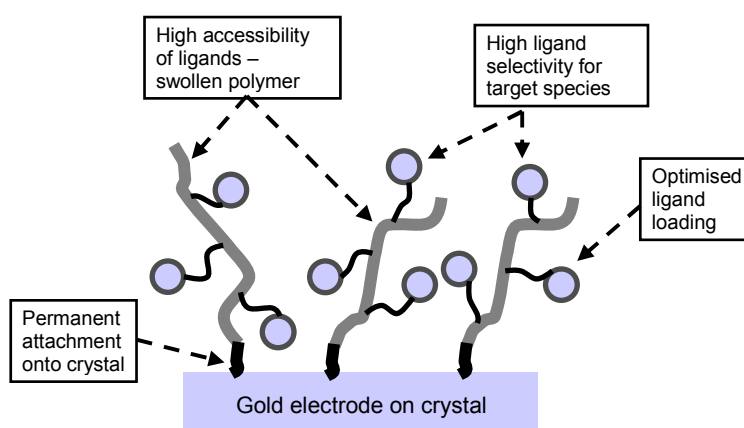


Figure 1. The design criteria for a polymer based piezoelectric sensor

The approach that has been adopted in our laboratory involves coating the crystal with a functionalised polymer to target metal ions in aqueous solution. This places a number of design criteria on the polymers to be used, as shown in Figure 1. The polymer must, of course, contain the appropriate functional group to interact with the analyte and this must be at an optimum level. Coating a crystal with a functional monolayer would be relatively straightforward but the use of a functionalised polymer means that a large loading can be obtained per unit area of the crystal. To ensure that the functionality remains accessible to the analyte, the coating should be compatible with the solvent; to prevent dissolution it is therefore necessary to anchor the

polymer to the crystal surface. All of these demands require careful design of the polymers and hence careful targeted synthesis. This should give improved sensitivity and speed of response over systems where the chelator is simply dissolved in an insoluble matrix such as PVC.

The success of our general approach was demonstrated by the development of polymer based QCM sensors for Cu^{2+} [10] and for Ni^{2+} [11, 12] with detection limits in the region of 0.1 ppm and reasonable, although not optimised, selectivity. Another potential target is the analysis of Group I metal ions so that it was decided to investigate sensors based on crown-ether containing copolymers. The metal-ion binding properties of a number of crown-ether copolymers were investigated by Kimura *et al.* [13] who showed that the copolymers reflect, and in some cases enhance, the binding properties of the free crown-ether rings. For this reason the polymers used in this work were based on those employed by Kimura *et al.* The crown-ether moieties selectively chelate the metal ion with an ionic radius compatible with the diameter of the crown-ether ring [14]. This selective chelating potential has been well documented since the pioneering work carried out by Pedersen [15] in the mid 1960's.

This paper describes initial work aimed at the synthesis and characterisation of several crown ether containing acrylic acid copolymers, determination of their ion-binding properties, strategies for their coating onto piezoelectric crystals as well as initial characterisation of their sensing behaviour.

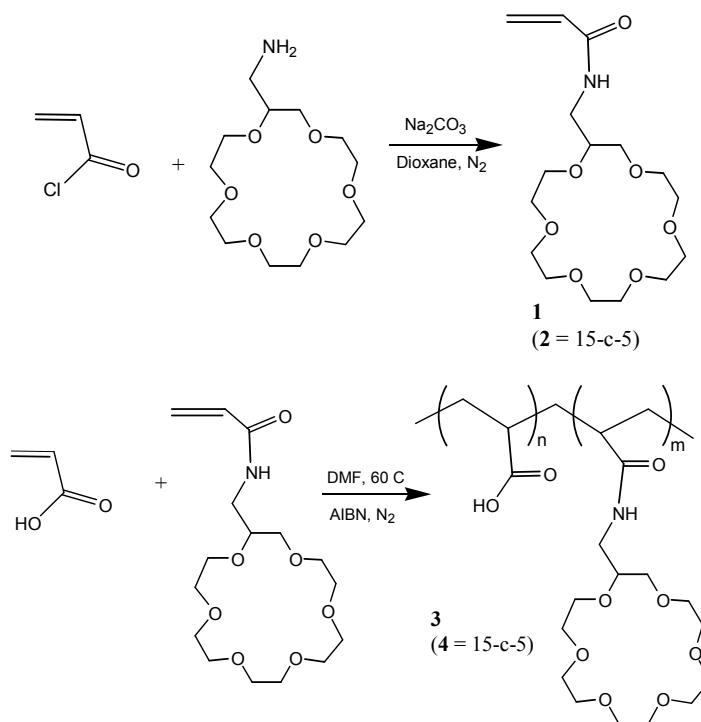
2. Experimental

2.1 Monomer and polymer synthesis

All compounds were obtained from Aldrich Ltd except where indicated. NMR spectra were recorded in CDCl_3 on a Varian 400 mercury system spectrometer. Mass spectrometry and elemental analysis were conducted on a Micromass VG autospec and CarloErba 1106 respectively. For characterisation of the sensor behaviour, all glassware was carefully washed

with 2M sulfuric acid and rinsed using Milli-Q_{plus} 185, 18.2 MΩ water. Milli-Q_{plus} water was also used to make up all aqueous stock solutions. GPC analysis was carried out a PL GPC-210 using DMF as the solvent and poly(methylmethacrylate) as the standard.

The synthesis is shown in Scheme 1.



Scheme 1. Crown ether containing monomer and polymer synthesis

Synthesis of acrylamidomethyl 18-crown-6, **1**. A solution of 1g of aminomethyl-18-crown-6 in 25 cm³ of freshly distilled 1,4-dioxane was stirred with 3g of dry NaCO_3 under N_2 . After 10 minutes, 0.5g of acryloyl chloride was added dropwise and the solution stirred for 3 hr before removing the NaCO_3 by filtration. The solvent and excess acryloyl chloride were removed via vacuum distillation at 40 °C leaving a 96% yield of a viscous yellow oil. The product was refrigerated and stored under nitrogen. Under these conditions the monomer was stable for approximately 2 weeks after which time some precipitate formed, assumed to be from auto-polymerisation.

¹H NMR [H_x at 5.5 ppm, H_a and H_b at 6.2 ppm (where $\text{RH}_a\text{C}=\text{CH}_x\text{H}_b$). alkene protons, doublets,

integration 2.7, $J_{xb} = 2.6$ Hz, $J_{xa} = 9.7$ Hz, $J_{ab} = 17.0$ Hz. 3.2-3.8 ppm multiplet, ring protons, integration 25]

^{13}C NMR [165 ppm C carbonyl, 130 ppm CH, alkene, 125 ppm CH_2 , alkene, 70-65 ppm CH_2 ring, 40 ppm CH_2 amine].

FAB mass spec $(\text{M}+\text{H})^+ = 348.2$ [calculated = 348.4].

CHN: found: 55.2C, 8.3H, 3.9N [calculated for $\text{C}_{16}\text{H}_{29}\text{N}_1$ 55.3C, 8.4H, 4.0N]

Synthesis of acrylamidomethyl 15-crown-5, 2. The same procedure used for **1** was followed which yielded 80% of 15-crown-5 monomer by using the equivalent 15-c-5 compound.

^1H NMR [6.8 NH proton integration 1. 6.1, 6.2, 5.6 ppm alkene protons, mutliplet/doublet, integration 3. 3.4-3.8 ppm multiplet, ring protons, integration 19]

^{13}C NMR [166 ppm C carbonyl, 132 ppm CH alkene, 126 ppm CH_2 alkene, 72-66 ppm CH_2 ring, 42 ppm CH_2 amine].

FAB mass spec $(\text{M}+\text{H})^+ = 304.2$ [calculated = 304.2].

CHN: found: 53.0C, 7.6H, 3.6N [calculated 53.1C, 7.9H, 4.4N]

Synthesis of poly(acrylamido-18-c-6)-co-(acrylic acid), 3. In a typical procedure, AIBN (0.07 g) and acrylic acid (3.2 g) was dissolved in dry DMF (20 cm^3) at 0 °C under N_2 . A DMF solution of 18-c-6 monomer **1** (0.90 g in 5 cm^3) was added the mixture heated to 60 °C for 2.5 hours. Ice cold methanol (40 cm^3) was added to quench the reaction and the copolymer was recovered by precipitation into diethyl ether and filtration. Yields of the copolymer were 70 - 72 %.

^1H NMR [4-3 ppm multiplet, crown-ether ring protons; 3.8-1.8 ppm multiplet. copolymer backbone protons].

^{13}C NMR [180 ppm C carboxylic acid, 70 ppm CH_2 crown-ether ring, 43 ppm CH copolymer backbone, 35 ppm CH_2 copolymer backbone].

CHN: 49.9C, 6.3H, 1.9N [calculated 51.5C, 6.7H, 2.0N].

FTIR [3800-2800 cm^{-1} OH (carboxylic acid), 1876-1700 cm^{-1} C=O (carboxylic acid), 1700 cm^{-1} C=O (amide), 1642 cm^{-1} N-H bend, 1500-1200 C-H bend, 1104 cm^{-1} C-O str, 951 cm^{-1} C-N str].

GPC [M_n 37500 *versus* PMMA standards in DMF].

Synthesis of poly(acrylamido-15-c-5)-co-(acrylic acid), 4. The same procedure as with **3** was used substituting **2** for **1**. The synthesis proceeded as before with the copolymer recovered in ~ 70 % yield.

^1H NMR [3.8-3 ppm multiplet, crown-ether ring protons; 3.8-1.8 ppm multiplet, copolymer backbone protons].

^{13}C NMR [180 ppm C carboxylic acid, 70 ppm CH_2 crown-ether ring, 42 ppm CH copolymer backbone, 35 ppm CH_2 copolymer backbone].

GPC [M_n 31500, *versus* PMMA standards in DMF].

Synthesis of the Cross-Linked Copolymer Resin. A typical procedure was to dissolve 0.9g of **1** or **2** with 7g EGDMA, 2g acrylic acid and 0.1g AIBN in 200 cm^3 acetonitrile under N_2 . The solution was stirred at 65 °C for 24 hours during which an opaque white solution formed. The precipitate was recovered by filtration following the addition of 50 cm^3 of ice cold methanol. The polymer was washed separately with methanol, diethyl ether, chloroform and water in a soxhlet for 24 hours and dried at 80°C. Yields of resin were in the range of 90 - 95%. A “blank” copolymer was synthesised by following the same procedure, omitting the crown ether.

Seven cross-linked resins with 10% w/w crown ether and various crosslink densities were prepared as shown in Table 1.

2.2 Metal ion absorption experiments

Stock solutions of 50 ppm of Na^+ (aq), Li^+ (aq) and K^+ (aq) were prepared from Analytical grade

materials. Aliquots of 50 cm³ of the stock solutions were placed into volumetric flasks and 1g of the precipitated, cross-linked resin added. Concentrations of the metal ions were measured using Atomic Emission Spectroscopy (AES) on a Varian AA275 instrument.

2.3 Preparation of sensor crystals

The piezoelectric crystals were 10MHz, AT-Cut, quartz crystals (ICM Co, Inc, Oklahoma City, Oklahoma) with 15 mm diameter quartz discs and 4.5 mm diameter circular electrodes (50Å Cr under-layer covered with 1 µm gold layer) on either side. The electronic driving circuits were built in-house and have been described previously [10]. They operate by comparing the frequency of a crystal with that of a reference crystal, the frequency difference being monitored.

Crystals were cleaned prior to use with piranha solution (1:1 ratio of 98% sulphuric acid and 40% H₂O₂), and rinsed with Milli-Q water. After drying, the resonance frequency was recorded and this used as the 'clean' frequency.

The crystals were coated by dipping into 30 cm³ of a 5 mM solution of 2-aminoethanethiol in ethanol until the resonant frequency became stable. The resonator was rinsed, dried and the resonance frequency again recorded. Depending on the coating methodology, 0.5 cm³ of the monomer or polymer mixture was dropped into a reaction well on the QCM resonator. The monomer mixture was the same as those used to prepare the cross-linked resins diluted with acetonitrile. The crystals were then heated to 75 °C for several hours to polymerize the monomers. After cooling the coated crystals were rinsed with hot acetonitrile followed by hot methanol and the resonance frequency recorded. They were then set in a mount where one face was sealed into a glass chamber so that only one side of the crystal came into contact with the solution.

2.4 Characterisation of sensor behaviour

The coated crystal was placed in a mount [10] in 30 cm³ of pure water and allowed to stabilise. Metal ions were then added to the water via the injection of a metal sulphate stock solution (10 – 100 ppm) and the change in resonance frequency followed. The sensor could also be operated in a flow system but the results reported here refer to operation in static mode.

3. Results and Discussion

Considering the design criteria illustrated in Figure 1, the ion selectivity is realised by the choice of crown-ether ligands which selectively bind Group I ions. The second requirement is achieved by basing the coating material on poly(acrylic acid), a highly water-soluble polymer which will swell in water. PAA also has two advantages; the monomers can be readily derivatised via simple amide or ester chemistry to aid the incorporation of the crown-ether groups and also facilitate metal ion adsorption by providing added donor sites and charge neutralisation. Attachment to the crystal is also facilitated by the remaining acid groups which can react with the surface via thiols.

3.1 Synthesis of the Copolymers

A range of copolymers was synthesised containing varied loadings of crown ether functionalities. Attempts to incorporate > 20% of 1 or 2 in the reaction mixture resulted in low yields of poor quality materials. Copolymers with either crown ether used displayed the same solubility in DMF, pyridine and DMSO although both only swelled in water and methanol. Spectroscopic methods confirmed the structure to be that illustrated. The GPC chromatograms of the two crown-ether containing copolymers are compared with an unfunctionalised poly(acrylic acid) sample synthesised under identical experimental conditions in Figure 2. The functionalised materials appear to have significantly higher molecular weights and polydispersities but this may

be an artefact of the PMMA calibration and changes in hydrodynamic volume promoted by incorporation of relatively large amounts of the crown-ethers which will modify the hydrophilicity of the polymer.

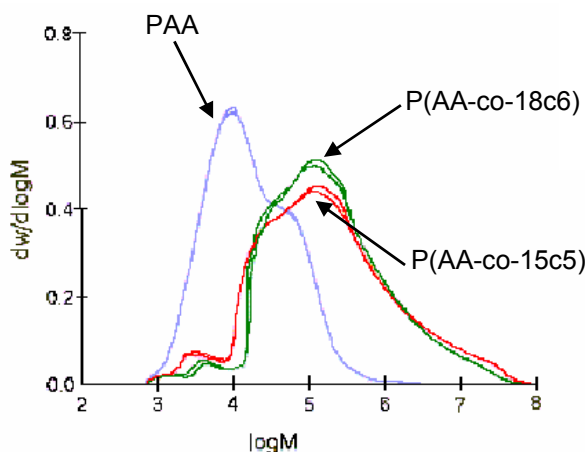


Figure 2. GPC chromatograms of poly(acrylic acid), (PAA), and two crown ether (10%) containing copolymers.

Several methods were utilised in order to attach the polymer to the surface of the crystal. A variety of thiols are known to adsorb irreversibly to the gold surface but an important feature was that the gold must be cleaned prior to reaction. The most elegant way of producing our sensor coating would be to adsorb a thiol containing an initiating species which could be used to grow the polymer from the surface. However, for this proof-of-principle work, the surface was coated with a thiol onto which preformed, acid containing copolymers could be attached.

A self-assembled monolayer of aminoethanethiol was formed [16], effectively converting the gold into an amino-functionalised surface onto which the copolymers could anchor by amide formation. On heating with a solution of the copolymer, 3 or 4, a frequency shift of around 2200 Hz corresponding to a mass of approximately 1.6 μg occurred, around 20 \times the change associated with the monolayer formation. All attempts to dissolve the copolymer film failed. The gold electrodes on the surface of the resonator are very thin and any vigorous cleaning techniques such as polishing and ultrasonic etching damage the electrodes rendering the

resonator inoperative. We are therefore confident that the polymer film is present and adheres to the resonator surface.

However, it was found that only relatively small amounts of polymer could be attached to the crystal using this method. While the polymer layer was not easily removed, the uptake selectivity between Li, Na and K was poor. Presumably, a given chain can interact with a number of surface sites, limiting the coverage of polymer. Also, to get appreciable reaction between polymer and coating, the system was heated to 130 °C and it is possible that some degradation of the crown ether functionality occurred. An alternative approach was therefore adopted involving the formation of the aminothioliol layer on the crystal followed by polymerising a solution of the monomers on the crystal. The result was a film permanently adherent to the resonator surface.

The amount of polymer coating the crystal is too small for meaningful analysis of its absorption properties so that measurements of ion uptake were conducted on samples of crosslinked copolymer resins with the same overall composition. Each of the recovered resins was a white powder, all seven being visually similar. After filtering, washing and drying, the percentage yield was typically 85 - 99 % and no unreacted **1** or **2** could be recovered from the reaction mixture. An example SEM is shown in Figure 3 and shows a relatively narrow

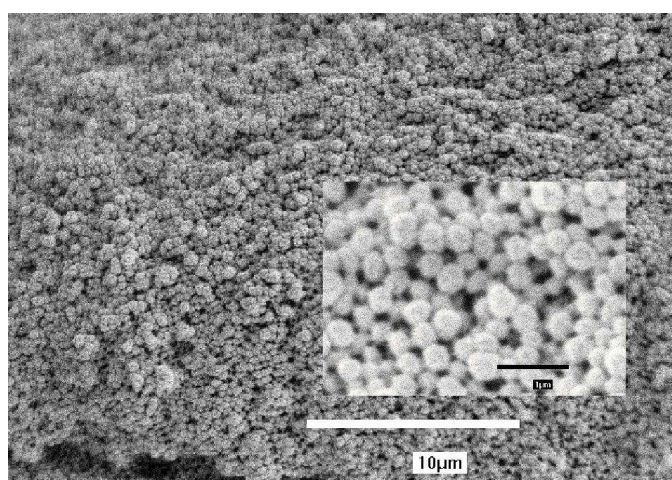


Figure 3. SEM images of PAA-15-c-6 resin. (The black bar in the inset represents 1 μm)

distribution of sizes. The unfunctionalised resin mainly comprised particles $\sim 380 - 450$ nm in diameter with just a few larger particles. The two crown-ether containing resins were somewhat more polydisperse; that containing **2** was mainly in the range $0.26 \mu\text{m}$ to $0.57 \mu\text{m}$ but with some larger ($1.2 - 1.3 \mu\text{m}$) particles present while the resin based on **1** was in the range $0.23 - 0.66 \mu\text{m}$ with no larger particles. These particle sizes are comparable but rather larger than the film thickness on a coated crystal.

The polymers satisfy our design criteria in that they carry a high level of functionality, contain free acid groups which allow further modification and are hydrophilic in nature so that they swell in aqueous solution. They can also be formed into adherent films of the quartz crystals. We therefore proceeded to characterise the metal ion uptake and sensor behaviour.

3.2 *Chelating ability of the copolymers*

The equilibrium absorption of Li^+ , Na^+ and K^+ from aqueous solutions is shown in Figure 4. The polymer powders were pre-swollen in water following which sufficient metal ion solution was added to give an overall concentration of 50 ppm. The change in solution concentration with time was monitored by atomic emission spectroscopy. Monitoring the rate of ion uptake showed that the absorption was complete within 2 minutes.

All of the resins absorbed $\text{K}^+_{(\text{aq})}$ to a greater extent than $\text{Na}^+_{(\text{aq})}$ or $\text{Li}^+_{(\text{aq})}$. The resins containing 18-c-6, show the largest uptake of K^+ , in the region of $1 \text{ mg K}^+_{(\text{aq})}$ per gram of copolymer. This is expected from the better match in cavity size. 18-c-6 has a ring diameter of $2.6\text{-}3.2 \text{ \AA}$ [17] compared with the K^+ diameter of $\sim 2.7 \text{ \AA}$ [17] so the K^+ ions bind more effectively and are retained in the copolymer network. Na^+ by comparison has a diameter of $\sim 1.8 \text{ \AA}$ and Li^+ a diameter of $\sim 1.2 \text{ \AA}$ so these ions are not bound as strongly. Significantly, the degree of crosslinker included in the copolymerization has little effect on the absorption of ions.

While the resins containing 15-c-5 have some affinity for $K^+_{(aq)}$ they have significantly larger $Na^+_{(aq)}$ uptake than the equivalent 18-c-6 network. The cavity size of 15-c-5 is $\sim 1.7\text{-}2.2 \text{ \AA}$, too small for the $K^+_{(aq)}$ ion to form a strong stable complex. The free 15-c-5 compound forms a 2:1 complex with $K^+_{(aq)}$ that has a stability constant in water of 0.74 compared to the 18-c-6 K^+ stability constant of 2.03 [18].

The results also show that the unfunctionalised resin has only very limited uptake capacity, presumably due to some ion-exchange effect, but no selectivity for the ions involved here. The acrylic-acid EGDMA copolymer is not capable of chelating the metal ions to any significant extent.

The calculated K^+ / Na^+ selectivity is 13.1, 13.1 and 13.8 for the three 18-c-6 containing copolymers in comparison with 3.6 – 4.3 for the 15-c-5 resins and 2.1 for the resin containing no crown ether. The first of these is therefore much more selective.

In practical use as a sensor, it is unlikely that solutions of single ions would be analysed so that it is important to investigate the competitive order to study the selective uptake of the copolymers. Figure 5 shows the results for absorption from a solution containing all three ions. It can be seen that the polymer containing no crown ether again absorbs no significant amount of any ion. The 15-c-5 polymers absorb similar amounts of $Na^+_{(aq)}$ and $K^+_{(aq)}$ from the single solutions (Figure 4) but only the latter is involved in competitive absorption. Also, for 18-c-6, when both $Na^+_{(aq)}$ and $K^+_{(aq)}$ are available for chelating only $K^+_{(aq)}$ is taken up. This further confirms the selectivity of both copolymers for $K^+_{(aq)}$ over $Na^+_{(aq)}$. The selectivity does not depend on the mass of copolymer used, as illustrated by Figure 6. The selectivity for absorption of K^+ over the other ions is maintained with varying amounts of resin. Again the capacity of the 18-c-6 material to act selectively is clearly demonstrated.

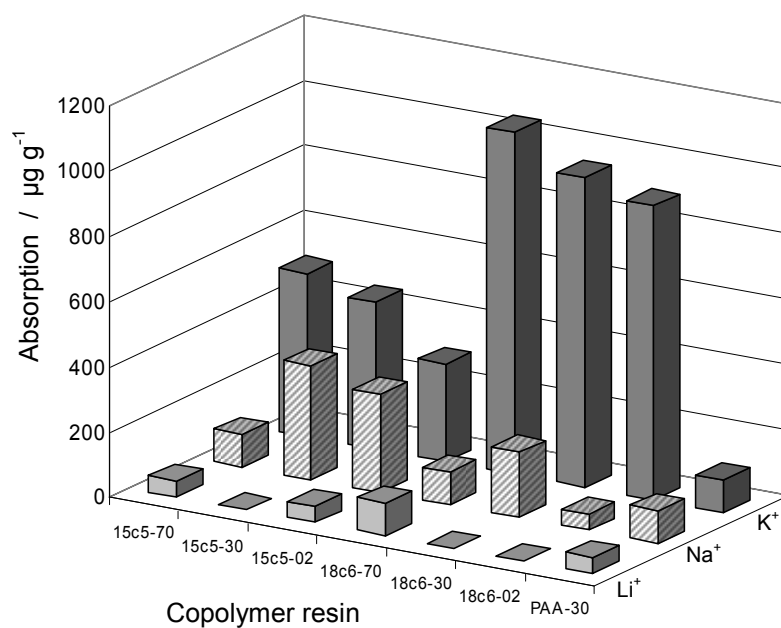


Figure 4. The uptake of aqueous metal ions by the crown ether copolymer resins

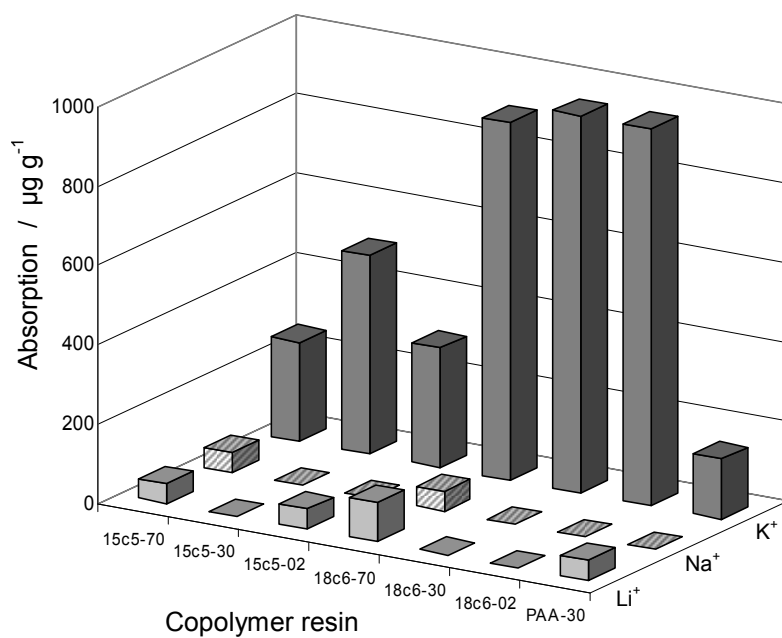


Figure 5. The competitive uptake of ions from a solution containing 50 ppm of each ion

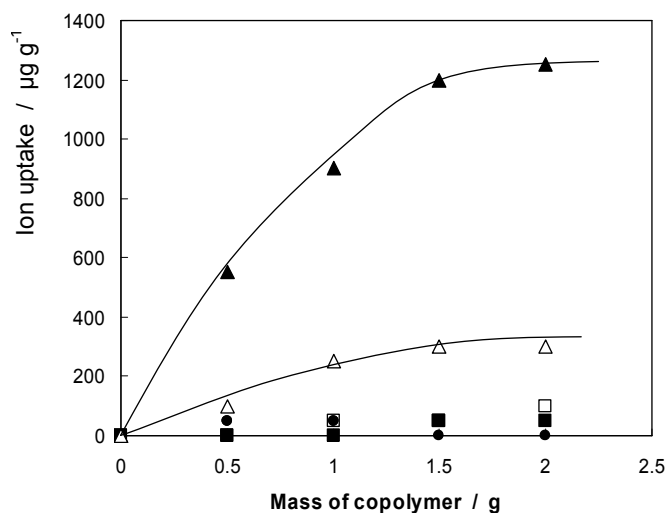


Figure 6. The competitive uptake of ions as a function of the mass of the resin. \blacktriangle , \triangle K^+ ; \blacksquare , \square Na^+ ; \bullet , \circ Li^+ . filled points, 18c6-30; open points 15c5-30

The equilibrium uptake by 0.5 g of 18c6-30 copolymer is shown in Figure 7 as a function of metal ion concentration. Similar profiles were obtained for varying masses of each of the crown containing copolymers and are characteristic of equilibrium adsorption processes. The uptake of the metal ions can be modelled by a Langmuir type isotherm where each crown ether is equivalent to an adsorption site. This isotherm assumes that every adsorption site is equivalent

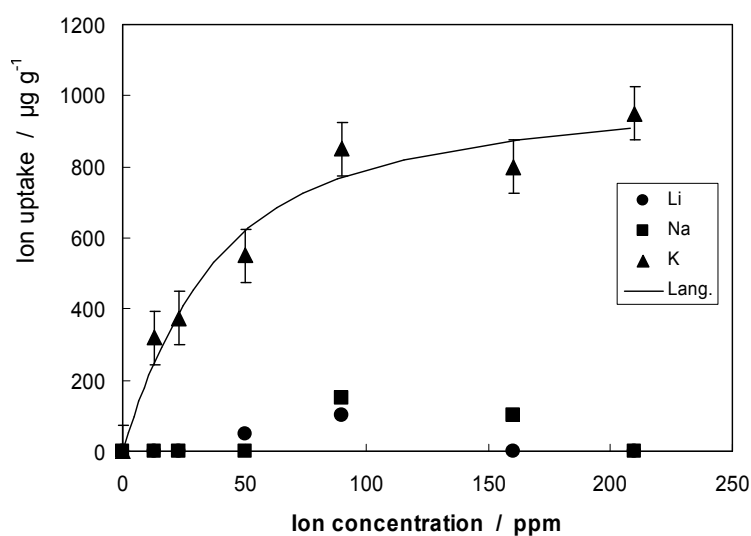
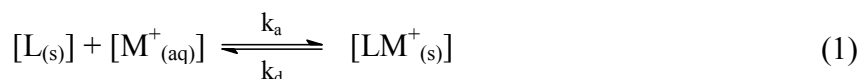


Figure 7. Ion uptake as a function of concentration.

and that the ability of a species to bind is independent of the occupancy of a surrounding site.

While these conditions, particularly the former, may not be strictly applicable here, it does allow more detailed characterisation of the adsorption. The fit of the Langmuir prediction to the data in Figure 7 is reasonable.

The adsorption equilibrium can be defined by:



where $[L_{(s)}]$ is the concentration of the uncomplexed crown-ether rings in the polymer, $[M^+_{(aq)}]$ is the concentration of the free metal ions in solution and $[LM^+_{(s)}]$ is the concentration of ion complexed crown-ether. k_a and k_d are the rate constants for the adsorption and desorption respectively. The fractional occupancy, θ , is therefore given by:

$$\theta = \frac{[LM^+_{(s)}]}{[L_{(s)}]} \quad (2)$$

The Langmuir isotherm can be expressed as

$$\frac{\theta}{(1-\theta)} = K[M^+_{(aq)}] \quad (3)$$

where K is the equilibrium constant for the adsorption. Substituting in (2) and rearranging gives:

$$\frac{[M^+_{(aq)}]}{[L_{(s)}]} + \frac{1}{K[L_{(s)}]} = \frac{[M^+_{(aq)}]}{[LM^+_{(s)}]} \quad (4)$$

which yields a linear relation from which the total number of binding sites available in the polymer and the equilibrium constant can be estimated.

The plots of Equation (4) for both systems studied are shown in Figure 8. The slope is inversely proportional to the number of available binding sites which is higher in 18-c-6. The reason for this is not clear since the degree of crosslinking was the same in both materials. The results suggest that only a small fraction, in the region of 20 – 40% of the total crown ether functionality included in the polymers participated in adsorption although this figure must be treated with caution due to the deficiencies in the model used. Inevitably, not all rings will be

equally accessible or energetically equivalent. However, it is clear that not all of the functionality incorporated into the polymer was useful and further optimisation is necessary. The values of the equilibrium constants are comparable with those quoted for other crown-ether systems [17, 18]. The values ($\log_{10}K$) that were calculated here are 3.3 and 3.7 for the 15-c-5 and 18-c-6 copolymers binding $K^+_{(aq)}$. The constants for the 18-c-6-metal ion complex in water are 0.8 and 2.03 for $Na^+_{(aq)}$ and $K^+_{(aq)}$ respectively [247]. The value calculated for the 18-c-6 $K^+_{(aq)}$ complex suggests that the copolymer has an increased affinity for $K^+_{(aq)}$ compared with to the free crown-ether compounds

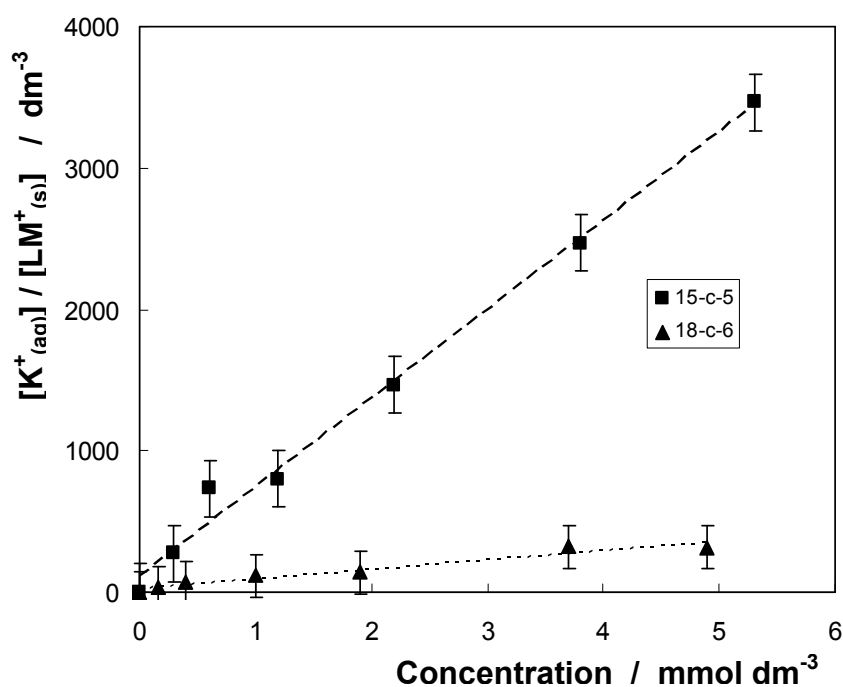


Figure 8. Langmuir plots for adsorption of K^+ by crown ether containing copolymers

3.2 Application of the copolymers as a sensor

Having established that the 18-c-6 containing copolymers display a high degree of selectivity for $K^+_{(aq)}$ and a fast response time, it was considered suitable for further study as a potential sensor.

Two copolymer coatings were investigated; an 18-c-6 copolymer based on the composition of resin 18c6-30 and a 'blank' copolymer containing no crown-ether based with the same degree of

crosslinking. They were coated from solutions with concentrations controlled so as to give film thickness in the region of 70 - 200 nm. Thicker films caused overloading of the crystals in our current configuration.

The change in resonance frequency is usually ascribed to a change in mass loading of the crystal. Sauerbrey [19] developed a theoretical description of the crystal oscillation that led to Eqn. (1) to describe the linear change in frequency, ΔF due to an increase in mass, M

$$\Delta F = (F_o^2 / A N \rho_q) M \quad (5)$$

where F_o is the fundamental oscillation frequency of the quartz crystal, A is the active area of the gold, N is a constant for the particular grade of quartz and ρ_q is the density of quartz. While it is well known that Equation (1) is at best an approximation [20], it is adequate so long as the frequency change is limited to $< 0.02 F_o$ and the fluid in which the crystal operates causes low acoustic loss. Frequency changes may also result if the incorporation of metal ions changes the viscoelastic properties of the swollen network. In this work, an additional complication arises due to the conducting solution. To eliminate conductivity effects, the crystal mountings were coated in non-conducting polymer. The reference crystal was also placed in an identical mount and included in the solution to cancel any other effects.

The response of a copolymer coated crystal to addition of K^+ ions in solution is illustrated in Figure 9. The crystal was allowed to stabilise in 30 cm³ water and 10 μ L injections of a stock solution were made, each injection adding 2.3 μ mol and changing the concentration by 3 ppm. The resonance frequency increased instantaneously by about 10 Hz for each successive injection. To ensure rapid mixing, a magnetic stirrer was used but the stirrer speed had no effect on the value or stability of the resonance frequency.

Figure 10 shows the response of the 18-c-6 functionalised QCM to addition of the three metal ions. There is negligible response to $Li^+_{(aq)}$ or $Na^+_{(aq)}$ but $K^+_{(aq)}$ produces a pronounced, reproducible response. From the slope of the plot, a response factor of 0.68 Hz ppm⁻¹ can be

calculated. Assuming a totally optimised frequency stability of ± 0.50 Hz this gives an estimated sensitivity of 0.1 ppm for the current system. As a control, the experiment was repeated using a polymer coating containing no crown ether, the results being shown in Figure 11. This clearly shows that the crown ether is necessary, the unfunctionalised polymer showing no affinity for any of the ions investigated and that the binding properties of the crosslinked copolymers

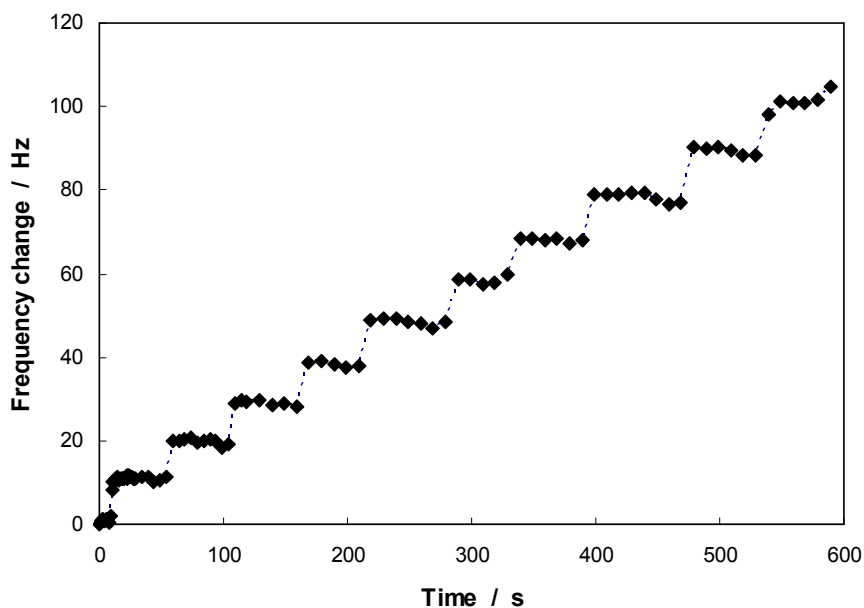


Figure 9. The response of 18-c-6 functionalised QCM to successive additions of $2 \mu\text{mol K}^+$ to 30 cm water.

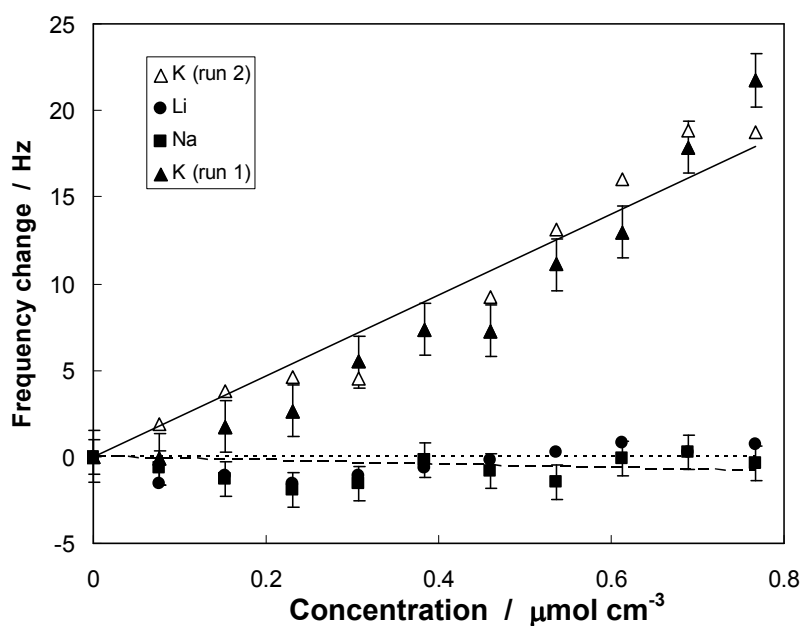


Figure 10. Concentration dependence of 18-c-6 functionalised QCM frequency change on addition of metal ions.

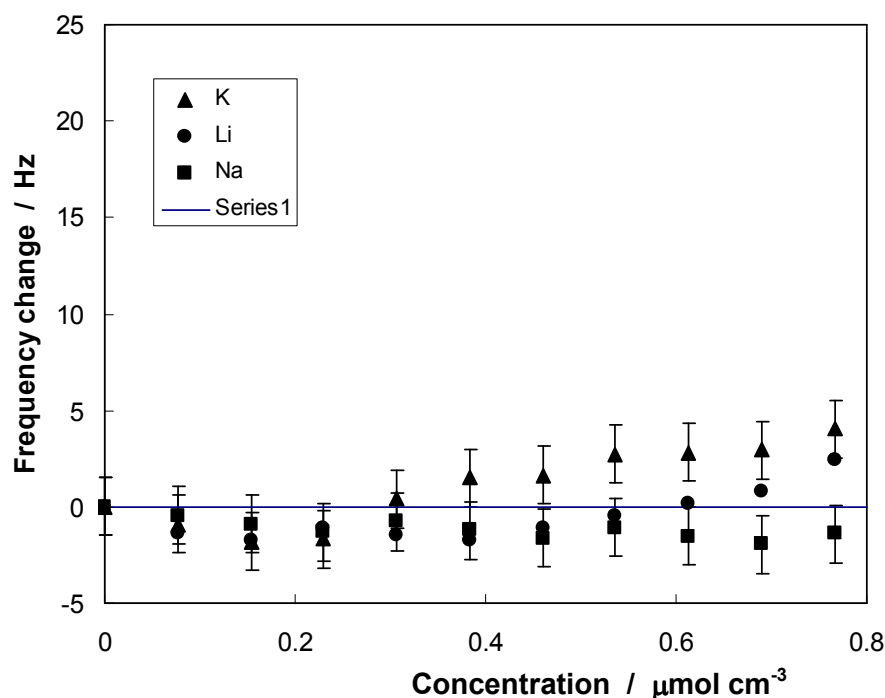


Figure 11. Concentration dependence of unfunctionalised QCM frequency change on addition of metal ions.

discussed above were successfully transposed to the QCM.

To investigate the range over which the sensor could be used, the results shown in Figure 12 were recorded. The $\text{K}^+_{(\text{aq})}$ response rises linearly up to a concentration of ~ 35 mM, corresponding to a solution of ~ 1350 ppm and plateaus thereafter, presumably due to saturation of the available adsorption sites.

The results were fitted to a Langmuir model as discussed above. However, the fit was less satisfactory than with the crosslinked resins and suggested that a range of different adsorption sites were in the polymer film. From a mechanistic point of view this could be explained if the cation penetration and binding to the copolymer coating proceeds slowly at first but increases with time as more and more ions penetrate the network; effectively acting in a co-operative nature to encourage ion binding. Analysis of the results allowed estimation of the equilibrium constant, $\log_{10}K = 3.1 \pm 0.3$ which is comparable with but rather lower than that for the bulk resin.

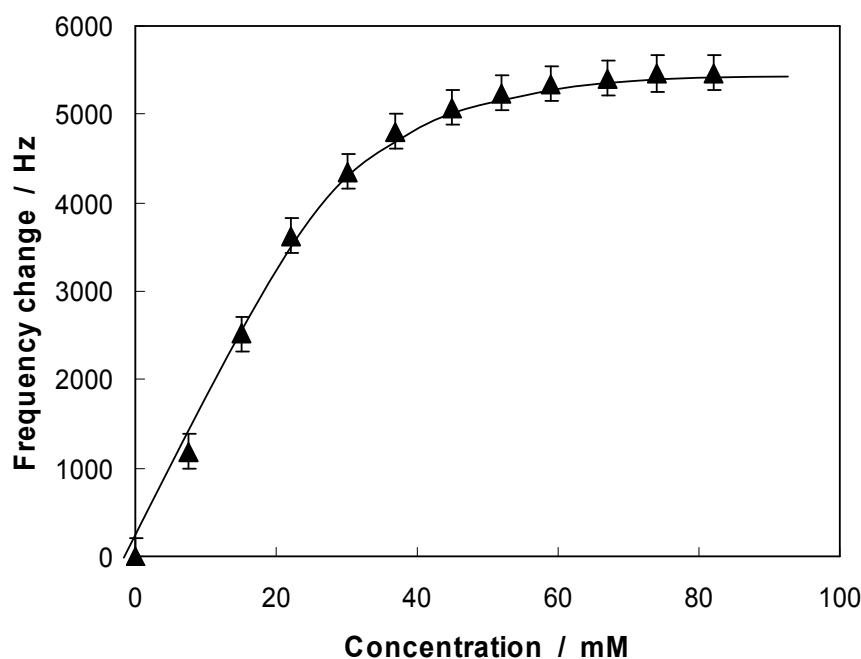


Figure 12. Concentration dependence of 18-c-6 functionalised QCM frequency change on addition of K^+ ions.

For the purpose of the work carried out in this paper the precise origin of the frequency response is of limited interest. The important observation is that a reproducible response exists and that this response is associated with the presence of the functionalised polymer. The relationship between frequency change and absorbed mass will not be straightforward over a large concentration range and will not be given to any degree of accuracy by Equation (1). However, the system is easily calibrated by measuring the response to solutions of known concentration, akin to the use of a pH meter or other ion-selective electrode.

The selectivity and sensitivity of this method are comparable with methods such as ion-selective electrodes. Optimisation of the coating in terms of the level of crown ether gives an avenue to increase the sensitivity. Although all the results here have been obtained in a “batch” mode, piezoelectric sensors are ideal for flow systems and the systems described here have been shown to operate with comparable sensitivity and selectivity with the results described in this paper [21].

4 Conclusions

Acrylic acid based crown-ether containing copolymer systems have been synthesised and shown to preferentially bind $K^+_{(aq)}$ in the presence of the other Group I ions $Na^+_{(aq)}$ and $Li^+_{(aq)}$. The 18-crown-6 containing material was coated onto a QCM resonator and used as a $K^+_{(aq)}$ sensor. The sensor developed had an estimated detection limit of 0.2 ppm and a linear response range of 0-1000 ppm with zero response to either $Na^+_{(aq)}$ or $Li^+_{(aq)}$. These values are well within the operating criteria for commercial K^+ sensors. The markets for such devices are in the areas of water analysis and physiological sensors. The concentration of K^+ in tap-water is typically in the range of 1-80 ppm. In the human body the concentration of K^+ in blood serum is around 140 ppm and bile around 500 ppm with the most common interference arising from Na^+ .

This is the first account of a crown-ether based copolymer being employed with the QCM as a selective cation sensor. It brings together the innovative use of a water compatible copolymer system with the QCM transducer for application in an aqueous environment. It has been demonstrated that such an approach is suitable to the development of liquid phase QCM based sensors and that such sensors possess the required selectivity and stability to operate in the ppm range. With improved design this range could be extended down to one part in 10^9 . The copolymer system incorporated in the sensor design can be readily modified to include a variety of different host compounds and offers a general route to the production of an array of selective chemical sensors.

The lifetime of the sensor also needs further investigation. The use of different cleaning procedures such as acid washing or even washing with a free crown-ether solution may help to regenerate the sensor after exposure to concentrated $K^+_{(aq)}$ solution. It would also be interesting to alter the sensing conditions such as temperature and pH. As well as being important from a commercial point of view these would also enhance the understanding of the binding and recognition mechanism involved.

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Table 1. Composition* of the acrylic acid based chelating resins.

Resin	Crown ether	% Crown-Ether #	% EGDMA	% Yield
15c5-70	18-c-6	8.1	70 %	84 %
15c5-30	18-c-6	11.4	30 %	99 %
15c5-2	18-c-6	13.3	2 %	82 %
18c6-70	15-c-5	10.8	70 %	74 %
18c6-30	15-c-5	13.4	30 %	69 %
18c6-2	15-c-5	11.4	2 %	83 %
PAA	-	0	70 %	94 %

* all percentages are based on w/w values.

the loading of crown ether in the recovered polymer was $\pm 2\%$

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