

## Adsorption, Preconcentration and Separation of Lead Ions by Novel Calix[4]arene Tetracarboxylic Acid Based Polyvinyl Resin

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### ABSTRACT

A novel resin has been synthesized through the polymerization of *p*-vinylcalix[4]arene followed by introduction of carboxyl groups at lower rim and adsorptive behavior of some divalent metal ions on the resin has been studied. Absolute separation of trace amount of lead from large excess of zinc has been achieved using the column packed with the resin.

**Keywords:** *p*-vinylcalix[4]arene tetraacetic acid resin, ion exchange, adsorption, lead ion, column chromatography

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### INTRODUCTION

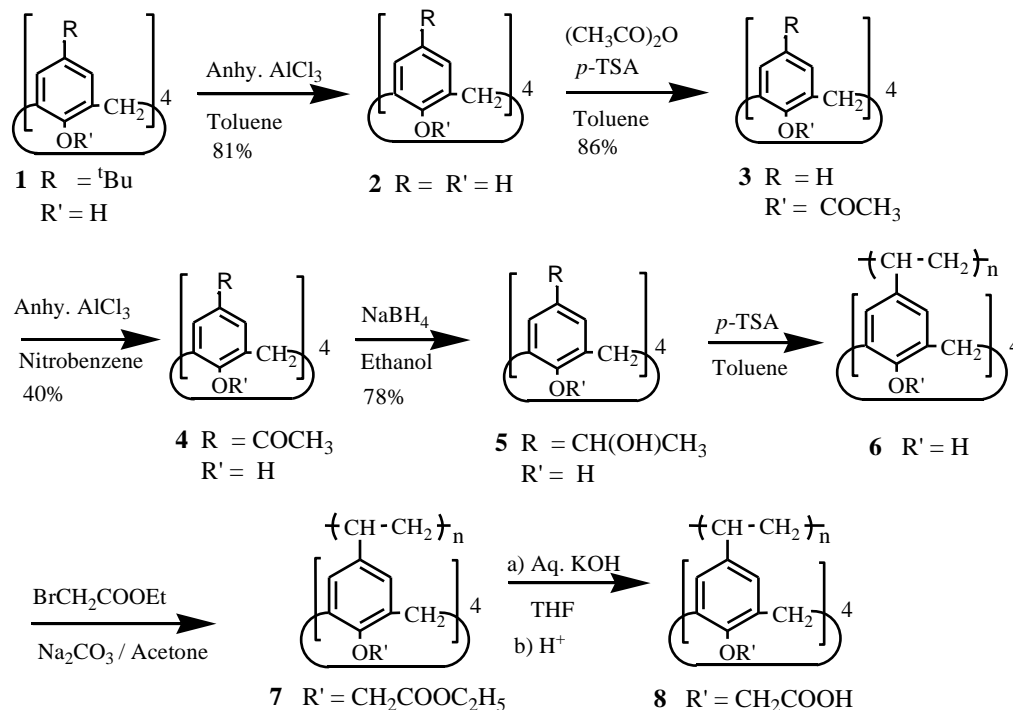
Despite being known as one of the prominent class of macrocycles for complexation with metal ions, poor dissolution of calixarenes in organic diluents is a major obstacle for employing them as solvent extraction reagents at industrial scale. Hence, apart from the considerable interest in use of calixarene monomers as platforms for construction of supramolecular receptor assemblies, in recent years, the growing interest has shifted to calixarene-based polymers. Consequently, some useful methods towards their incorporation into polymeric matrices have been exploited, either by covalent linking<sup>1</sup> or blending to them.<sup>2</sup> Previously, we had proposed four different kinds of calixarene-based resins namely impregnated resin, polymer supported resin, cross-linked resin and vinyl polymerized resin<sup>3</sup>. We and several other groups have already reported the metal complexation behavior of the first three kind of resins<sup>1,2,4-6</sup>. Only a few papers have been reported for the fourth kind of resin. Blanda *et al.*<sup>7</sup> reported the synthesis of vinyl copolymers containing pendant calix[4]arene units through radical initiated reactions involving a vinylic calix[4]arene monomer respectively with methylacrylate, acrylonitrile and styrene. Miloshev *et al.*<sup>8</sup> reported the copolymerization of calixarene having isopropenyl groups and styrene by radical polymerization reaction. However, to the best of our knowledge, no paper has been reported regarding the homopolymerization of calixarene units through vinylic polymerization. In an extension of previous studies, hopefully to develop

the resin with high selectivity for lead ions as that of lead ion imprinted polymers<sup>9</sup> and high loading capacity than the previous resins, we decided to synthesize the fourth resin through vinylic polymerization. In this communication, we report the synthesis of vinyl polymerized calix[4]arene tetracarboxylic acid resin and its adsorption behavior towards some toxic metal ions.

### EXPERIMENTAL

The compounds 5,11,17,23-tetra-*t*-butyl calix[4]arene-25,26,27,28-tetrol **1** and calix[4]arene-25,26,27,28-tetrol **2** were synthesized according to the literature procedure<sup>10</sup>. *O*-Acetylation followed by Fries rearrangement and reduction<sup>11</sup> of **2** yielded the compound 5,11,17,23-tetrakis(1-hydroxy)ethylcalix[4]arene-25,26,27,28-tetrol **5** (Scheme 1). Dehydration of **5** with *p*-toluene sulfonic acid took place with subsequent polymerization<sup>12</sup> and afforded the calix[4]arene resin **6**. Carboxyl groups were introduced at 'lower rim'<sup>13,14</sup> of **6** based on the reported procedure.<sup>15</sup>

The adsorption experiments were carried out according to batch and column methods. In batch experiment, aqueous solutions were prepared by dissolving individual metal nitrates into 0.1 M (M= mol dm<sup>-3</sup>) HCl and 0.1 M HEPES [2-{4-(2-hydroxyethyl)-1-piperazinyl} ethanesulphonic acid] buffer solution. These solutions were arbitrarily mixed to adjust the desired concentration (0.1 mM) and pH. The resin (0.02 g, particle size 75 μm or



Scheme 1 Synthesis of resin 8

less) was added to 10 cm<sup>3</sup> aqueous solution and stirred at 303K for more than 10 h.<sup>16</sup> After equilibrium, metal ion concentration and equilibrium pH were measured by atomic absorption spectrophotometer (AAS, Shimadzu AA-6500) and a pH meter (Beckman, Φ45), respectively. In column experiment, the aqueous feed solution was prepared by dissolving zinc and lead nitrates into 0.1 M nitric acid solution. The initial pH of aqueous solution was adjusted to 3.8 and the concentrations of zinc and lead were 300 and 5 ppm, respectively. The feed solution was passed through the packed bed of 0.15 g of resin supported by glass beads. Once the adsorption was completed, the resin was washed with distilled water and the adsorbed metal was eluted with 1 M nitric acid. In both the breakthrough and elution experiments, the feed rate was 5.45 cm<sup>3</sup> h<sup>-1</sup>. The metal concentrations in the collected sample solutions were determined by AAS.

## RESULTS AND DISCUSSION

Experimental results of pH dependency on the adsorption behavior of Pb (II), Co (II), Ni (II), Cu (II) and Zn (II) ions on **8** are shown in Figure 1. The logarithms of formation constant for metal carboxylate (acetate) complexes of Pb (II), Cu (II), Zn (II) and Co (II) ions under similar conditions are reported to be 1.43, 2.23, 1.57 and 1.46 respectively<sup>17</sup>. Hence, based on their association constant value, the carboxyl group

should be more selective towards Cu (II) rather than Pb (II). However, the resin has interestingly high selectivity for lead ion. The results are attributable with size fitting of lead ion into the calix[4]arene cavity<sup>18</sup> and coordinating effect of oxygen rich carboxyl function coupled with ion exchange phenomenon.

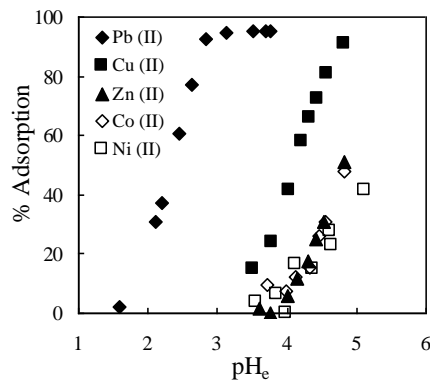
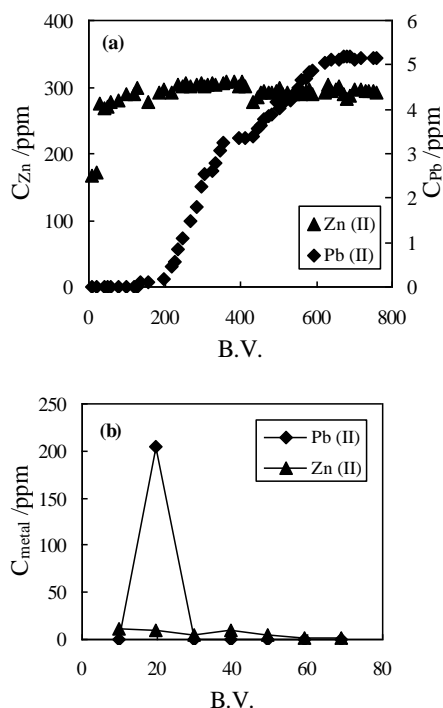


Figure 1. Effect of equilibrium pH on percentage adsorption of different metal ions on **8**. [metal ion] = 0.1 mM; 0.1 M HCl-0.1 M HEPES.

Since the resin shows strong selectivity to lead over copper, zinc, cobalt and nickel ions, it is reasonable that the present resin is suitable for the removal of trace amount of lead from large amount of other metals, mainly copper, zinc, cobalt and

nickel. By means of breakthrough followed by elution using the packed column, small amount of lead ion should be adsorbed on resin leading to preconcentration and separation from the excess amount of zinc ion. The breakthrough profiles of lead and zinc are shown in Figure 2 (a). As expected from the results of batch experiment, breakthrough of zinc ion was immediately observed after the starting of the feed without being trapped in the bed. On the contrary, the breakthrough of lead began to take place after as late as about 200 bed volume (B.V.). This clearly suggested that the complete separation of trace amount of lead from zinc was successfully achieved by using a column packed with resin **8**. The elution profiles of the loaded metal ions from the column with 1 M nitric acid are shown in Figure 2 (b). A very sharp elution profile of lead is observed at about 20 B.V., which demonstrates that preconcentration factor of lead was 200 times compared with the feed solution. On the other hand, the elution of zinc ion is in negligible quantity compared with that of lead. These results are promising in the sense that the present resin would be useful in achieving selective and effective removal and recovery of trace amount of lead from the polluted water, soil and industrial effluents.



**Figure 2.** (a) Breakthrough and (b) elution profiles of lead and zinc ions.  $[Pb^{2+}] = 5$  ppm;  $[Zn^{2+}] = 300$  ppm, flow rate  $5.45 \text{ cm}^3 \text{ h}^{-1}$ , pH of feed solution 3.8 (adjusted with 0.1M  $HNO_3$ , 0.1 M HEPES buffer), eluent 1 M  $HNO_3$ .

## CONCLUSIONS

We have prepared a novel resin based on vinylic polymerization of calixarene units. The resin selectively adsorbs lead ion at pH 2.5 to 3.5. The loaded lead is easily eluted with acid solution. In the prospect of high lead selectivity and repeated use after adsorption followed by elution, the resin holds promise for cleansing lead polluted water and industrial effluents.

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- Compound **3** was obtained as needle like pale yellow crystals.  $^1H$ -NMR (300 MHz,  $CDCl_3$ , TMS)  $\delta$  1.54 (s, 12H,  $CH_3$ ), 3.75 (s, 8H, Ar- $CH_2$ -Ar), 7.03-7.2 (m, 12H, ArH) indicates that it is in 1,3 alternate conformation. Compound **4** was obtained as a brown powder.  $^1H$ -NMR  $\delta$  2.49 (s, 12H,  $CH_3$ ), 3.73 (s (br), 4H, Ar- $CH_2$ -Ar, *exo*), 4.26 (s (br), 4H, Ar- $CH_2$ -Ar, *endo*), 7.75 (s, 8H, ArH), 10.16 (s, 4H, OH) suggests that it is in cone conformation. Compound **5** was obtained as a brown powder.  $^1H$ -NMR  $\delta$  1.37 (d, 12H,  $CH_3$ ), 2.31 (s (br), 4H, alcoholic OH), 3.50 (s (br), 4H, Ar- $CH_2$ -Ar, *exo*), 4.24 (s (br), 4H, Ar- $CH_2$ -Ar, *endo*), 4.66 (m, 4H, CH), 7.05 (m, 8H, Ar-H), 10.21 (s ,4H, Ar-OH) confers that it is in cone conformation.
- Dehydration of **5** is similar to the dehydration reaction of 1-phenylethanol to styrene. US patent no 3526674 describes the use of *p*-toluenesulphonic acid as a dehydrating agent for such reaction. However, in

our case, the product obtained by treating **5** with *p*-TSA was not soluble in any organic diluent in which the calixarene monomers are usually soluble. Hence, it was predicted that dehydration occurred with subsequent polymerization and afforded the polymeric resin **6**, which was further supported by the IR spectra of resins.

13. In cone conformation of calixarene, all the hydroxyl groups are facing one side and this constitutes the lower rim of calixarene backbone. Since the polymer precursor is in cone conformation, it is reasonable that calix[4]arene maintains the cone conformation on polymeric resin too. Therefore, the phenolic group of resin is also regarded as the 'lower rim' in this communication.

14. The percentage yield of carboxylate groups was determined by neutralization titration as well as pH titration experiments. The number of millimoles of NaOH required for complete neutralization of 1 g of resin is found to be 44.5 which is roughly equal to the number of millimoles of carboxyl groups if all the phenolic groups of resin are modified with carboxyl

groups. Hence, 100% yield of carboxyl groups on the resin was achieved.

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16. Our results of kinetic experiment on lead adsorption (unpublished data) indicate that more than 85% of the total adsorption takes place within 15 minutes of shaking under same conditions of batch experiment. Adsorption rate increases with time and a plateau is reached after 8 h. Since ion exchange mechanism mainly takes place, complete wetting of gel in aqueous medium is required to facilitate the dissociation of proton which, because of hydrophobic nature of resin, is relatively slow and takes few hours. Thus it was assumed that at least 10 h shaking is required in order to achieve the equilibrium.

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