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SEPARATION SCIENCE AND TECHNOLOGY, 37(8), 1943–1958 (2002)

ADSORPTION BEHAVIOR OF LEAD ION ON CALIX[4]ARENE TETRACARBOXYLIC ACID IMPREGNATED RESIN

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ABSTRACT

The resins impregnating calix[4]arene tetracarboxylic acid into XAD-7 has been prepared to investigate adsorption behavior of lead ion. The leakage of the impregnated reagent to an aqueous solution is found to be negligible. The sequence in the adsorptive selectivity series for divalent metal ions on the present resin is as follows: Pb $\gg$ Cu $>$ Zn $>$ Ni $\approx$ Co. This sequence is also the same with that of the extractive selectivity series of *p*-*t*-octylcalix[4]arene as an extractant. The other adsorption properties of the resin for metal ions are similar to the extractive properties of the corresponding calix[4]arene tetracarboxylic acid. Maximum adsorption capacity of lead ion on the resin is found to be $0.33\,\mathrm{mol\,kg^{-1}}$. For endurance test, even in eight times repetitive experiment of adsorption followed by elution of lead, the resin is devitalized and available for repeatability. Column chromatographic separation of lead and zinc ions as an industrial

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application is also carried out. Selective adsorption of trace amounts of lead ion over excess amount of zinc ion is achieved.

Key Words: Calix[4]arene carboxylic acid; Impregnated resin; Adsorptive separation; Lead ion; Column chromatography; Repetition test

INTRODUCTION

Since the development of novel resin containing macrocyclic compounds, first in 1971 by Feigenbaum and Michel (1), various resins containing crown ethers (2–5) and cryptands (6–9) have been prepared.

Calixarenes are phenolic cyclic oligomers with very attractive and interesting host compounds (10,11). A number of studies have been conducted on ion recognition in homogeneous phase and liquid–liquid systems (12–16). The authors have been also attracted to the ion recognition by calixarenes and have employed these compounds as solvent-extraction reagents (17–24) to find their specific extraction behavior. However, in spite of the attractive extraction behavior, these compounds suffer from some serious disadvantages as solvent extraction reagents such as poor lipophilicity. The poor solubility in organic diluents impedes their extensive use as extractants on a commercial scale. In order to improve those disadvantages, the authors synthesized highly lipophilic calixarene compounds with α-symmetric structures having different alkyl chains (25), which, however, improved the solubility only to a limited extent, and therefore, was not a breakthrough to resolve the lethal disadvantage. An option to avoid these drawbacks and to effectively make use of the characteristic properties of calixarenes as ionophores with high recognition ability is to use them as solid chelating ion exchangers. Although the development of novel types of resins incorporating macrocyclic ligands has considerably advanced over the recent years as described above, there are not many articles for the resins incorporating calixarenes (26–34). Although these resins exhibit excellent adsorption properties, their preparation is not easy because it needs multi-step syntheses and the yields are low.

There are two types of the so-called reagent-incorporated or solvent-impregnated resins based upon different methods of preparation (35–37). The first approach is based on physical adsorption. That is, the extractant is retained in the micropores of an inert polymer without any chemical bonds onto the polymer matrix (38). The second approach, which is named as the Levextrel resin, is in situ incorporation of the extractant during the copolymerization process. The merits of such resins are easy preparation, high yield and high selectivity (39), and a wide choice of reagents with desired selectivity and simplicity in adjustment of the amount of the impregnated extractant (35,36). The extraction properties of the impregnated extractant are responsible for the adsorption properties (38,40,41). Owing to such advantages, the development of impregnated resins containing calixarene derivatives appears to be of great interest. Although Hutchinson et al. reported on the adsorption properties of some metal ions on a resin in which calix[4]arene hydroxamate was impregnated in Amberlite XAD-4 (27), the details of the effect of the calixarene derivative has not been studied.

In our previous work, we reported the preparation of the calix[4]arene carboxylate resin incorporated onto polymer matrices of polyallylamine (42). The resin showed high lead selectivity, though the preparation was complex and required multi steps. We also reported the preparation of the solvent-impregnated resins using various carboxylate derivatives of phenolic oligomers, such as cyclic hexamer, cyclic tetramer, linear trimer, and monomer derived from *p*-*t*-octylphenol as the impregnating reagents, and macroporous Amberlite XAD-7 resin as the polymer matrices as well as their adsorption behavior for various metal ions (44). Among them, the resin impregnated with calix[4]arene tetracarboxylate showed the highest lead selectivity. However, this resin exhibited only poor loading capacity for lead, because the impregnated *p*-*t*-octylcalix[4]arene tetracarboxylate has a high molecular weight, which resulted in the lowering of calix[4]arene content per unit weight of the resin.

In the present work, we prepared some resins impregnated with carboxylate derivatives of *p*-*t*-butylcalix[4]arene and debutylated calix[4]arene in Amberlite XAD-7 to investigate adsorption behavior of some metal ions, especially for lead ion. From the practical point of view, leakage of the impregnated extractant into the aqueous solution, maximum loading capacity of lead ion, durability for many repeats of adsorption and elution of lead ion, as well as chromatographic adsorptive separation of lead and zinc were examined.

EXPERIMENTAL

Reagents

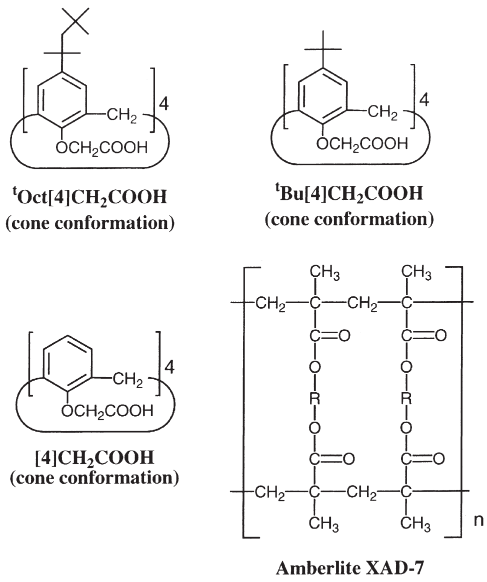
Cone conformational 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetra-*t*-butylcalix[4]arene (abbreviated as ^{t}Bu[4]CH_2COOH) (45,46), cone conformational 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene, (abbreviated as ^{t}Oct[4]CH_2COOH) (17), and cone conformational 25,26,27,28-tetrakis(carboxymethoxy)calix[4]arene (abbreviated as [4]CH_2COOH) (25) were synthesized according to the procedure reported in the previous papers.

Although a number of polymer matrices suitable for the preparation of impregnated resins have been reported, we employed Amberlite XAD-7, the average pore size, porosity, and specific surface area of which are 80 Å, 55%, and $450\,m^2\,g^{-1}$, respectively, produced from acyclic ester due to its polarity for impregnation of the extractants, large pore size, high porosity, and high specific surface area suitable for the present work.

The chemical structures of the impregnated extractants and the macroporous polymer matrix are shown in Fig. 1.

Preparation of the Impregnated Resins

Amberlite XAD-7 purchased from Organo Co., Ltd. was washed with methanol three times, followed by drying in vacuo (32). Each extractant (1.00 g) was dissolved in an analytical graded chloroform. The dried XAD-7 (3.00 g) was immersed in the organic solution overnight. The weight ratio of the extractant to XAD-7 was adjusted to 25% (weight of the extractant/weight of the dried macroporous resin), which is the maximum percentage of impregnation. After chloroform was removed in vacuo, this procedure was repeated several times. In



^{t}Oct[4]CH$_2$COOH (cone conformation)

^{t}Bu[4]CH$_2$COOH (cone conformation)

[4]CH$_2$COOH (cone conformation)

Amberlite XAD-7

Figure 1. Chemical structures of the impregnated extractants and macroporous polymer matrix.

general, the percentage of the impregnation is equal to the porosity of the macroporous matrix. Since the porosity of XAD-7 is 55%, the impregnation percentage should be about 50% (45). However, it was only 25% for the present resin, which is attributed to the fact that the impregnated calix[4]arene compound itself possesses spacious cavity.

Leakage of the Impregnated Extractant in Aqueous Phase

Aqueous solutions were prepared by arbitrarily mixing 0.1 mol dm^{-3} hydrochloric acid and 0.1 mol dm^{-3} 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) buffer solution to adjust the initial pH. To 50 cm^3 of the aqueous solution was added 0.10 g of the impregnated resin and the mixture was shaken at 303K for 24 hr. After filtration, up to 100 cm^3 of concentrated or diluted hydrochloric acid solution was added to the filtrate to alter the pH to a value around 1. To the solution, 5 cm^3 of chloroform was added to extract and concentrate the leaked extractant by 10 times. The concentration of the extractant extracted in chloroform was measured by means of UV/VIS/NIR spectrophotometry (Perkin Elmer, LAMBDA 190).

Adsorption of Some Metal Ions

The adsorption experiments were carried out using the conventional batch method (31,32). A small quantity (0.1 mmol dm^{-3}) of aqueous metal solutions was prepared by dissolving individual metal chlorides into 0.1 mol dm^{-3} hydrochloric acid and 0.1 mol dm^{-3} HEPES buffer solutions, followed by arbitrarily mixing these solutions to adjust the pH. To 10 cm^3 of the solution was added 0.02 g of the resin, and the mixture was stirred for more than 10 hr at 30°C. After filtration, the metal concentration and pH of the aqueous solution were measured by atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 100, abbreviated as AAS) and a pH meter (Beckman, ϕ45), respectively. In the experiments to examine the repetition of lead adsorption, 0.02 g resin was added to the aqueous solution kept at a pH of 3.8. After adsorption, 0.1 mol dm^{-3} nitric acid solution was used as an eluent. The other procedures were similar to that of the pH dependency.

The elution tests of the loaded lead ion were carried out by contacting various concentration of aqueous nitric acid (10 cm^3) with the resin (0.02 g), which was washed by distilled water and dried prior to the elution, after the batchwise loading at 303K for more than 10 hr. After filtration, the lead concentration in the acid solution was measured by AAS and the eluted percentage of lead ion was calculated by mass balance.

Chromatographic Separation of Lead and Zinc Ions

In the column experiment, the aqueous feed solution was prepared by dissolving zinc chloride and lead chloride in dilute nitric acid solution, the pH of which was 3.6. The feed solution containing large excess of zinc (1000 ppm) and small amount of lead (10 ppm) was passed through the bed packed with the resin (0.28 g) mixed together with glass beads (0.1 g, average diameter = 1.3 mm). After washing with distilled water, the adsorbed metal was eluted with 1 mol dm^{-3} nitric acid. In both cases, the feed rate was 12.8 cm^3 hr^{-1}. The metal concentrations in the collected sample solutions were determined by AAS.

RESULTS AND DISCUSSION

Leakage of the Extractant in Aqueous Phase

As mentioned earlier, from practical point of view, the impregnated extractant in the resin should be completely retained during the use for a longer time. The effect of pH on the percentage leakage of the impregnated extractants, ^{t}Bu[4]CH_2COOH, ^{t}Oct[4]CH_2COOH, and [4]CH_2COOH, from the resins is shown in Fig. 2(a)–(c). Equation (1) gives the percentage leakage of the impregnated extractant.

$$\text{Leakage (\%)} = \frac{\text{amount of the leaked extractant in the aqueous solution}}{\text{total amount of the impregnated extractant in the resin}} \times 100 \qquad (1)$$

As shown in Fig. 2, calix[4]arene tetracarboxylates with alkyl radicals of *t*-butyl or *t*-octyl were found to hardly leak into the aqueous phase over the whole range of pH examined, while that with no alkyl radicals gradually leaked with increasing pH; especially at pH 5 the leakage was greater than 1%. The leakage may be attributed to acid dissociation and aqueous distribution of the extractant. Judging from the pH region at which Li and K are extracted with ^{t}Oct[4]CH2COOH, pK_{a1} of calix[4]arene tetracarboxylic acid may be about 3–3.5 (47). The sufficiently lipophilic ^{t}Bu[4]CH_2COOH and ^{t}Oct[4]CH_2COOH were found to get rid of the obvious leakage.

Adsorptive Distribution of Metal Ions on ^{t}Bu[4]CH2COOH-Impregnated Resin

The effect of shaking time on the amount of adsorbed lead on ^{t}Bu[4]CH_2COOH-impregnated resin is shown in Fig. 3, where the adsorbed

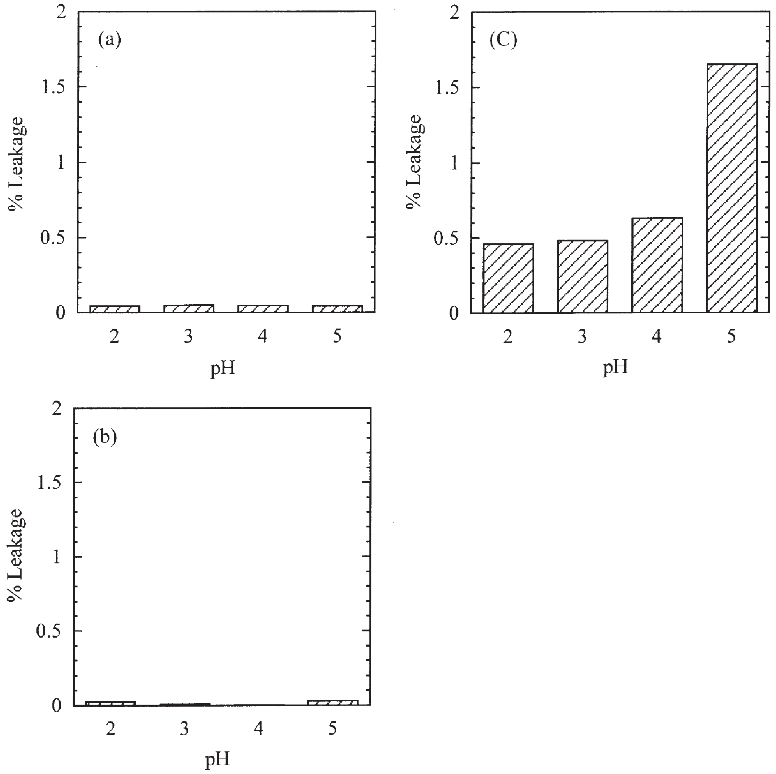


Figure 2. Effect of pH on percentage leakage of the extractant from the resin to aqueous solution: (a) ^{t}Oct[4]CH_2COOH, (b) ^{t}Bu[4]CH_2COOH, (c) [4]CH_2COOH.

amount, q (mol kg^{-1}), is defined by

$$q = \frac{C_i - C_e}{w} \times \frac{V}{1000}. \tag{2}$$

The time required for this resin to attain equilibrium was found to be 10 hr, while in our previous article, the time for ^{t}Oct[4]CH_2COOH-impregnated resin was found to be 24 hr (44). The slow adsorption rate is considered to be attributed to the hydrophobicity of the surface of the resin (45). Since the particle size and the impregnation percentage are almost the same for both the impregnated resins, the difference between ^{t}Bu[4]CH_2COOH- and ^{t}Oct[4]CH_2COOH-impregnated resins in the rate to reach equilibrium may be attributed mainly to the hydrophobicity.

The effect of pH on the distribution ratio of some divalent metal ions on ^{t}Bu[4]CH_2COOH- impregnated resin is shown in Fig. 4, where the distribution

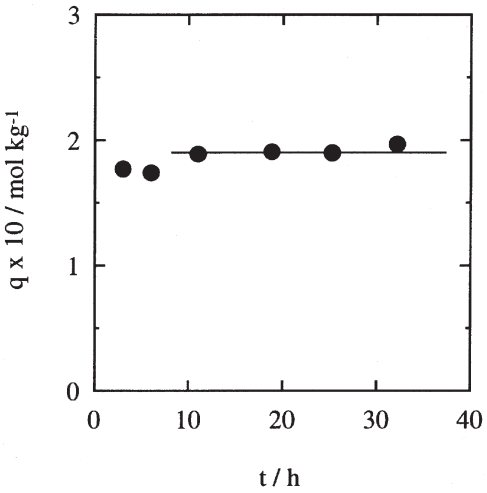


Figure 3. Effect of adsorption amount of lead ion on shaking time. Weight of ^{t}Bu[4]CH$_2$COOH-impregnated resin: 0.020 g, 0.1 mol dm^{-3} HNO$_3$–0.1 mol dm^{-3} HEPES, initial pH = 3.21.

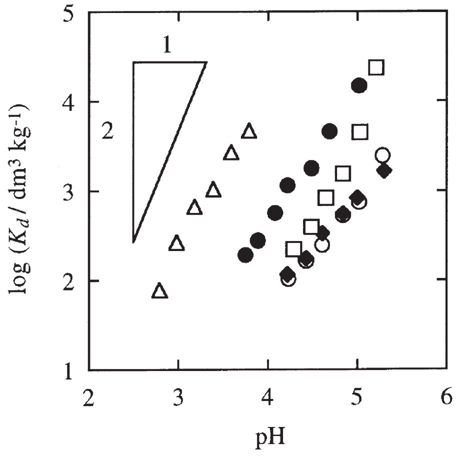


Figure 4. Effect of pH on distribution coeffeciency of metal ions on ^{t}Bu[4]CH$_2$COOH-impregnated resin. △: Pb(II), ●: Cu(II), □: Zn(II), ◆: Ni(II), ○: Co(II), Weight of ^{t}Bu[4]CH$_2$COOH-impregnated resin: 0.020 g, 0.1 mol dm^{-3} HNO$_3$–0.1 mol dm^{-3} HEPES.

coefficient, K_d ($dm^3\,kg^{-1}$), is defined by

$$K_d = \frac{q}{C_e}. \tag{3}$$

The plots of Pb, Cu, and Zn shown in Fig. 4 lie on straight lines with a slope of two. Since the slope of the plots corresponds the positive charge of metal ions, the metal ions are considered to be adsorbed by the general ion-exchange mechanism. However, the plots of Ni and Co lie along straight lines with a slope less than two. At high pH region, the adsorption of these metal ions may also be affected by ester groups in XAD-7.

The selectivity among the examined metal ions was almost the same for all resins, which is given as follows:

$$\mathrm{Pb} \gg \mathrm{Cu} > \mathrm{Zn} > \mathrm{Ni} \approx \mathrm{Co}.$$

This selectivity is in agreement with those for the impregnated reagent (24) and for the resins incorporated with the functional groups of calix[4]arene carboxylate (42–44). The specifically high selectivity of lead is attributed to the "size-fitting" effect between lead ion and calix[4]arene carboxylate, and the abundant sites of "hard" oxygens. Therefore, this selectivity originated nearly from the nature of the impregnated ^{t}Bu[4]CH_2COOH.

Adsorption of Lead on ^{t}Bu[4]CH_2COOH-Impregnated Resin

Since ^{t}Bu[4]CH_2COOH-impregnated resin shows the specifically high lead selectivity, adsorption of lead on ^{t}Bu[4]CH_2COOH-impregnated resin was examined in detail in terms of maximum loading capacity, elution test, repetition test, and chromatographic separation by using packed column.

The adsorption isotherm of lead on ^{t}Bu[4]CH_2COOH-impregnated resin is shown in Fig. 5. The amount of lead adsorption increases with increasing lead concentration and reaches a constant value that is the maximum adsorption capacity of the resin impregnated with ^{t}Bu[4]CH_2COOH, 0.33 mol kg^{-1}. The content of the impregnated ^{t}Bu[4]CH_2COOH was 25 wt%, corresponding to 0.28 mol kg^{-1}. Therefore, the maximum adsorption capacity of lead ion was found to be roughly equivalent to the theoretical content of calix[4]arene moiety, suggesting that the stoichiometry of lead and the impregnated ^{t}Bu[4]CH_2COOH is in the ratio 1:1. A similar result was also observed for ^{t}Oct[4]CH_2COOH-impregnated resin; in this case, the maximum adsorption capacity of lead ion and the theoretical content of calix[4]arene moiety were 0.28 and 0.23 mol kg^{-1}, respectively.

This maximum adsorption capacity appears to be insufficient for industrial use. However, negligible leakage and the effective separation are worth noting.

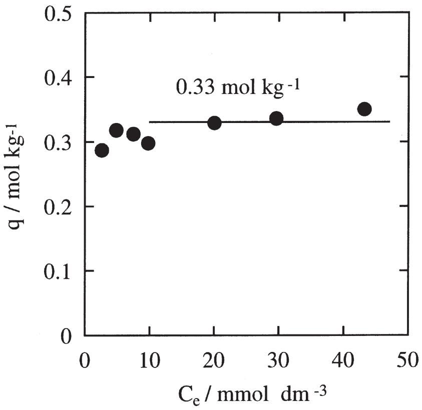


Figure 5. Adsorption isotherms of lead (II) on the impregnated resins. Weight of the resin: 0.010 g, volume of the solution: 10 cm^3, initial pH = 3.6.

Furthermore, as expected in the previous article (44), the low-loading capacity could be improved by exchanging the impregnating extractant from ^{t}Oct[4]CH_2COOH to calix[4]arene carboxylate with a lower molecular weight and by increasing the amount of the impregnated extractant molecule, although the lowest [4]CH_2COOH were not useful due to the large leakage from the resin to aqueous solution.

Prior to the repetition test and adsorptive separation of lead and zinc by column chromatography, the elution test of the loaded lead ion from ^{t}Bu[4]CH_2COOH-impregnated resin was examined. That is, it was carried out using various concentrations of nitric acid. Table 1 lists the relation between nitric acid concentration and elution percentage of loaded lead ion on the resin. The result shows that 0.1 mol dm^{-3} nitric acid was found to be enough to elute the loaded lead ion completely.

Table 1. Relation Between Concentration of Nitric Acid and Elution Percentage of Loaded Ion on ^{t}Bu[4]CH_2COOH-Impregnated Resin

[HNO_3] (mol dm^{-3})	Elution (%)
0.1	97.8
0.5	100.0
1.0	100.0
2.0	98.2

The relation between percentage adsorption and the repetitive number of adsorption followed by elution of lead ion on and from the resin was also investigated. The fact that the percentage adsorption of lead was kept at a higher extent of at least within eight times, suggests that the present resin can be used for adsorption repeatedly. The reason why the resin shows the excellent and long-term endurance is attributed to the negligible leakage of the impregnated extractant and the complete elution with dilute acidic solution.

Since the selectivity of the resin to lead over the other metal ions is superior to those of commercial resins, it can be concluded that it is suitable for the removal of trace amount of lead from large amount of other metals. For example, the waste solution of zinc plating contains trace amount of lead ion as a contaminant. Therefore,

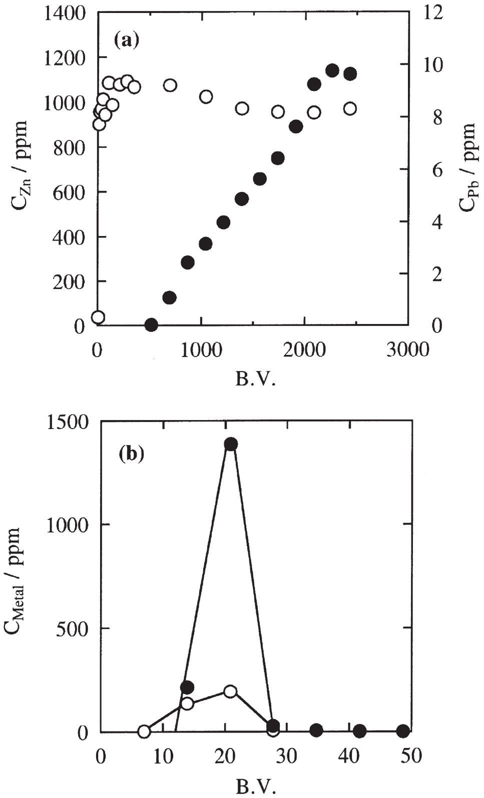


Figure 6. Breakthrough (a) and elution (b) profiles of lead (●) and zinc (○) ions. $[Pb^{2+}] = 10$ ppm, $[Zn^{2+}] = 1000$ ppm, Bed volume 0.92 cm^3, flow rate 12.8 cm^3h^{-1}, pH of feed solution: 3.6, elution solution: 1 mol dm^{-3} HNO_3.

a small amount of lead ion should be adsorbed on the resin and separated from the excess amount (100 times that of lead ion) of zinc ion by means of breakthrough followed by elution, using the packed column mentioned earlier to confirm actual separation efficiency. The breakthrough profile of zinc and lead are shown in Fig. 6(a). Bed volume (abbreviated as B.V.) represents the volume ratio of the solution that passed through column and the packed resin. As expected from the result of the batch experiment, zinc ion was immediately broken through 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 500 B.V. It is suggested clearly that the complete separation of trace amounts of lead from zinc can be achieved successfully by using a column packed with the resin impregnated with calix[4]arene carboxylic acid. The elution profiles of the loaded metal ions from the column with 1 mol dm^{-3} nitric acid are shown in Fig. 6(b). A very sharp elution profile of lead is observed at about 20 B.V., which demonstrates that lead can be concentrated by as much as 140 times of the feed solution. On the other hand, the elution of zinc ion is a very small quantity compared with that of lead. These results are promising in the sense that they suggest that the present resin might be useful in achieving a selective and effective removal of a trace amount of lead from the polluted water.

NOMENCLATURE

w (kg)	weight of dry resin
V (dm^3)	aqueous solution volume
C_i (mol dm^{-3})	initial concentration of metal ions in the aqueous solution
C_e (mol dm^{-3})	equilibrium concentration of metal ions in the aqueous solution
q (mol kg^{-1})	adsorbed amount
K_d(dm^3 kg^{-1})	distribution coefficient

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