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Ion exchange of ^{90}Sr and ^{137}Cs into 1-vinyl-2-pyrrolidone–divinylbenzene cation-exchange resin

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Radiotracer batch ion-exchange experiments were employed to investigate the uptake of ^{90}Sr and ^{137}Cs radioisotopes by various cation-exchanged forms of a 30% cross-linked macroporous 1-vinyl-2-pyrrolidone–divinylbenzene cation-exchange resin with 1.37 ml g^{-1} pore volume, 0.0232 μm pore diameter and 271.2 m^2 g^{-1} surface area. The uptake of ^{90}Sr and ^{137}Cs was determined by taking liquid aliquots at various time intervals from solutions over solids. The volume-to-solid ratio was kept at 200. The results of kinetic experiments for the carrier-free ^{90}Sr and ^{137}Cs were evident in all cationic forms of the resin. The percentage uptake and distribution coefficient K_d values with carrier (0.005 M $SrCl_2$ and 0.01 M CsCl) concentrations were also determined, and the best results were obtained from the Li^+ and H^+ forms of the resin. Cerenkov counting (β^--counting) was used to observe the initial and final radioactivity in the liquid phase. All the experiments were carried out at room temperature and the radioactivity in each case was corrected for the background counts. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: 1-vinyl-2-pyrrolidone–DVB resin; cationic forms; radiotracers; kinetics; K_d values; Cerenkov counting

INTRODUCTION

Poly(divinylbenzene-co-*N*-vinylpyrrolidone) copolymer has been used as a cation exchanger for the chromatographic separation of aromatic acids, aldehydes, phenols and/or supports for binding, e.g. iodine, hydrogen peroxide or phenols. It has a large number of various applications owing to its distinguished properties, such as high swelling pressure with water, being therapeutically inactive and physiologically inert. It is a macroporous, water-wettable, but insoluble, copolymer having the hydrophilic *N*-vinylpyrrolidone and the lipophilic divinylbenzene to provide the reversed-phase retention necessary to retain analytes. Therefore, it is more flexible at processing samples, since it can dry out during the extraction procedure without diminishing its ability to retain analytes. Moreover, the copolymer is chemically stable at high pH.[1–4]

Regardless of the role played by the matrix in determining the properties of an ion exchanger, the decisive factor is the ionogenic group. The strong acid cation exchangers with an ionogenic group consisting of sulfonic acid have attained much importance among the ion exchangers produced from a matrix of styrene with divinylbenzene as the cross-linking agent. These cation-exchange resins have been widely used in the nuclear industry for the removal various radioisotopes from nuclear waste streams. They have also been used in the chemical processing industry for strict environmental demands, pharmaceuticals, water treatment and in a number of other fields.[1–8]

From the beginning of the nuclear era, much attention has been paid to the determination of ^{90}Sr and ^{137}Cs because of their production in abundance with a nuclear fallout, health hazard nature and with both the nuclides having relatively long half-lives of ~30 years. Since ^{90}Sr behaves like calcium from a chemical point of view, its presence in the environment for a long time makes it an important radionuclide for man to deal with. The separation of ^{137}Cs from nuclear waste streams is also of major environmental concern, as if it is separated this can minimize the possible damage to man and the environment.

This investigation was stimulated by the need to find some suitable ion exchangers (organic and inorganic) for the removal of fission products as a part of radioactive waste treatment and containment studies. In this regard, the

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performance of a 30% cross-linked macroporous 1-vinyl-2-pyrrolidone–divinylbenzene cation-exchange resin in which sulfonic acid was incorporated into poly(divinylbenzene-co-*N*-vinylpyrrolidone) copolymer was assessed by carrying out some ion-exchange batch experiments for the selective removal of ^{90}Sr and ^{137}Cs nuclides, both in carrier-free and with carrier concentrations.[5]

EXPERIMENTAL

Materials and chemicals

1-Vinyl-2-pyrrolidone (97% purity) was supplied by Fluka Chemicals (Buchs, Switzerland); divinylbenzene (60% purity) was purchased from Reidel-de-Häen, Germany; benzoylperoxide (BPO), purchased from Fluka Chemicals, Switzerland, was used as initiator. Diethylphthalate (Reidel-de-Häen), dimethylphthalate (BDH, Poole, UK), dibutylphthalate (Merck, Darmstadt, Germany), and bis-2-ethyl hexylphthalate (dioctylphthalate; Fluka) were used as diluents. Gum arabic and gelatine (Fluka), were used as suspension agents. Sulfuric acid (98%) was obtained from Merck. All these chemicals were used as supplied.

The copolymerization was carried out by the usual suspension polymerization technique. The aqueous phase was prepared by dissolving 1.5 g each of gelatine and gum arabic and 3.0 g of NaCl in 150 ml of demineralized water (DMW). The organic phase was prepared by dissolving 0.3 g of BPO as initiator in 30 ml of monomer and diluent.

The organic phase was added slowly into the aqueous phase with constant stirring. The temperature of the vessel was increased to 80 °C and kept constant for 22 h. The reaction mixture was then refluxed for 2 h at 95–100 °C. The 1-vinyl-2-pyrrolidone–divinylbenzene copolymer obtained was washed with hot DMW and then with methanol until free from all the organics.

Sulfonation of the copolymer

The sulfonation of the original synthesized form of 1-vinyl-2-pyrrolidone–divinylbenzene copolymer was carried out by the following procedure: 10 g of the dried copolymer was mixed with 50 ml of sulfuric acid (98%) and the mixture was stirred for 3 h at 90 °C. This mixture was washed with DMW until it became free from all impurities. By this technique, a 30% cross-linked macroporous 1-vinyl-2-pyrrolidone–divinylbenzene resin was synthesized; other details can be found from the literature.[1,5]

The ^{90}Sr and ^{137}Cs radioisotopes were obtained from the Radiochemical Centre, Amersham International, UK.

Cation-exchanged forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin

The cation-exchanged forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin were obtained by treating the original synthesized form with the respective metal chloride/ammonium chloride salt solution in excess. The resin was filtered, washed with distilled water, dried for 4 weeks at room temperature, and kept in desiccators for further use.

Kinetic experiments

Kinetic experiments were carried out to check the percentage uptake of ^{90}Sr and ^{137}Cs with and without 'carrier' solution. A typical procedure was as follows: 20.0 ml solutions of each salt, traced with ^{90}Sr and ^{137}Cs radioisotopes, were equilibrated with 0.1 g of various cationic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin in separate polythene vials at room temperature. The vials were shaken and, at various time intervals, 10 ml of the supernatant solution was withdrawn and counted by Cerenkov counting in the tritium channel of a Packard model A-2700 liquid scintillation analyser for final radioactivity in the liquid phase. A window of 0–600 keV was set so as to cover the maximum energy range of beta rays emitted from ^{90}Sr (β^- decay; $E_{\max} = 546$ keV) and ^{137}Cs (β^- decay; $E_{\max} = 511$ keV) nuclides.

Radioisotope measurement

Percentage removal of ^{90}Sr and ^{137}Cs radioisotopes as a function of time for the cation-exchanged forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin was determined using

$$\text{Removal (\%)} = \frac{A_i - A_f}{A_i} \times 100 \tag{1}$$

where A_i is the initial activity and A_f is the final activity (cpm ml^{-1}) of the solution.

Distribution coefficient experiments

The distribution coefficient measures partitioning of ions between solid and liquid phases. It gives an idea of the affinity of ions towards the ion exchanger, or otherwise. The distribution coefficient K_d values were determined for ^{90}Sr and ^{137}Cs with and without 'carrier' (0.005 M $SrCl_2$ and 0.01 M CsCl) concentrations. The procedure was as follows: 20 ml solutions of each salt, labelled with ^{90}Sr and ^{137}Cs radioisotopes, were equilibrated with 0.1 g of 1-vinyl-2-pyrrolidone–divinylbenzene resin in plastic vials. The vials were rotated in a mineralogical roller for a maximum of 24 h. At equilibrium the vials were centrifuged and 10 ml of the supernatant solution in each case was withdrawn and counted by Cerenkov counting.

The distribution coefficients K_d (ml g^{-1}) values were calculated using

$$K_d = \frac{(A_i - A_f)V}{A_f W} \tag{2}$$

where A_i and A_f are as in Eqn (1), V (ml) is the volume of solution and W (g) is the weight of the resin.

RESULTS AND DISCUSSION

Kinetics of removal under carrier-free (CF) conditions

The preliminary kinetic experiments of carrier-free ^{90}Sr and ^{137}Cs showed that the rate of exchange in both cases was very fast. In almost all cationic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin, ~100% uptake of ^{90}Sr and ^{137}Cs was achieved. This provided an idea regarding the selectivity of the exchanger towards both the Sr^{2+} and Cs^+ cations in carrier-free conditions.

Removal of ^{90}Sr with 0.005 M carrier solutions

The kinetic experiments of ^{90}Sr with carrier concentration for various cationic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resins are given in Table 1. The results show that the rate of exchange is again fast even with carrier, and uptake is achieved within the first hour. The removal of ^{90}Sr was again observed in almost all the cationic forms of the resin as in the carrier-free condition. However, the rate of uptake of ^{90}Sr with 0.005 M $SrCl_2$ solutions for various cationic forms was in the order of

$$H^+ < Li^+ < Na^+ < K^+ < NH_4^+$$

and ranged from 79 to 98.5% uptake. This also showed that the cation-exchange capacity (CEC) obtained for strontium was equivalent to ~1 meq g^{-1} of the H^+ form (H_3O^+) of 1-vinyl-2-pyrrolidone–divinylbenzene resin. This suggests that, in future, we may be able to increase the CEC further for the Sr^{2+} ion by changing the cross-linking of the resin.

Removal of ^{137}Cs with 0.01 M carrier solutions

The kinetic experiments of ^{137}Cs with 0.01 M carrier solution are shown in Table 2. The results show that the uptake is observed in almost all the cationic forms of the 1-vinyl-2-pyrrolidone–divinylbenzene resin as in the carrier-free condition. However, the rate of uptake of ^{137}Cs with 0.01 M CsCl solutions was in the order of

$$H^+ < Li^+ < Na^+ < K^+ < NH_4^+$$

and ranged from 68 to 95.5% uptake. This also showed that the CEC for caesium obtained was equivalent to ~0.86 meq g^{-1} for the H^+ form (H_3O^+) of 1-vinyl-2-pyrrolidone–divinylbenzene resin.

Table 1. Uptake of ^{90}Sr with 0.005 M carrier solution by various cationic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin

Time (h)	Uptake (%) H^+ form	Li^+ form	Na^+ form	K^+ form	NH_4^+ form
1	93.0	92.5	90.5	80.0	79.0
2	94.0	93.0	92.0	81.0	80.0
5	96.0	95.6	93.0	85.0	83.5
24	98.5	97.5	96.0	89.5	85.5

Table 2. Uptake of ^{137}Cs with 0.01 M carrier solution by various cationic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin

Time (h)	Uptake (%) H^+ form	Li^+ form	Na^+ form	K^+ form	NH_4^+ form
1	80.0	78.5	75.5	70.0	68.0
2	82.0	80.0	78.0	75.0	74.0
5	86.0	85.6	83.0	77.0	74.5
24	95.5	92.5	86.0	84.5	80.5

Distribution coefficient values in the presence of carrier solutions

The preliminary kinetic experiments for the removal of strontium and caesium radioisotopes confirmed the fast exchange reaction of the resin; nevertheless, a 24 h equilibration time was given for the distribution coefficient experiments. In these experiments as both the ingoing cation, e.g. Sr^{2+} and Cs^+, and the concentration of the carrier solution were the same in each case, the differences in the K_d values obtained for both the nuclides may be due to the differences in the selectivity of ^{90}Sr or ^{137}Cs for the various cationic forms of the resin. The K_d values for carrier-free ^{90}Sr and with carrier solutions are shown in Tables 3 and 4 respectively. In both these cases the results of $H^+(H_3O^+)$, Li^+ and Na^+ forms of the resin were higher compared with the K^+ and NH_4^+ forms of the resin. This may be due to differences in the ionic sizes of more hydrated ions, e.g. Li^+ and Na^+ ions, compared with the least hydrated ions, e.g. K^+ and NH_4^+ ions. Horvath[9] states that the least hydrated potassium and ammonium ions are nearly identical in size (1.33 Å and 1.48 Å respectively), so the position of potassium and ammonium in the selectivity series quoted above is sensible. However, similar data on the hydronium ion are lacking. The better K_d values obtained for the H^+ form of the resin are unexplained.

The K_d values for ^{137}Cs with 0.01 M carrier concentration are shown in Table 5. The results of removal by H^+ (H_3O^+),

Table 3. K_d values of carrier-free ^{90}Sr onto homo-ionic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin in distilled water

Cationic form of resin	Ionic size (Å)	K_d (ml g^{-1})
H^+	1.41	29 100
Li^+	0.60	26 489
Na^+	0.95	25 200
K^+	1.33	22 260
NH_4^+	1.48	20 229

Table 4. K_d values for ^{90}Sr onto homo-ionic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin with 0.005 M $SrCl_2$ solution[a]

Cationic form of resin	Ionic size (Å)	K_d (ml g^{-1})
H^+	1.41	7300
Li^+	0.60	4500
Na^+	0.95	3075
K^+	1.33	1260
NH_4^+	1.48	1100

[a] The ionic radius of the ingoing cation Sr^{2+} is 1.13 Å.

Table 5. K_d values for ^{137}Cs onto homo-ionic forms of 1-vinyl-2-pyrrolidone–divinylbenzene resin with 0.01 M CsCl carrier solution

Cationic form of resin	Ionic size (Å)	K_d (ml g^{-1})
H^+	1.41	6106
Li^+	0.60	5895
Na^+	0.95	3905
K^+	1.33	2160
NH_4^+	1.48	2010

[a] The ionic radius of the ingoing cation Cs^+ is 1.69 Å.

Li^+ and Na^+ forms of the resin were higher than for K^+ and NH_4^+ forms of the resin. This may also be due to the differences in the ionic sizes of more hydrated ions, e.g. Li^+ and Na^+ ions, compared with the least hydrated ions, e.g. K^+ and NH_4^+ ions, as stated above. The better K_d value for ^{137}Cs obtained by the H^+ form of the resin is not in accord with this criterion and is not explained.

CONCLUSIONS

It may be concluded that the H^+ and Li^+ forms of 1-vinyl-2-pyrrolidone–divinylbenzene resins are more effective in removing ^{90}Sr and ^{137}Cs isotopes than the other cationic forms, both in carrier-free and with carrier concentrations.

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