# Cation Exchange Studies of Lithium on Dowex 50W-X8 Separation from Mixtures

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Cation exchange behaviour of lithium on Dowex 50W-X8 has been studied. Hydrochloric, nitric and sulphuric acid and chloride, bromide, iodide, nitrate and acetate of ammonium were tested as the eluants and their selectivity scale was devised. Lithium was separated from various elements by the process of selective or gradient elution or selective sorption. Some separations of common elements. were possible in the mixed solvent systems.

**M**OST of the work dealing with cation exchange chromatography of lithium has centred either around mixed solvent system[1] or its separations from other alkali metals or alkaline earths. Hydrochloric or nitric acid showed strong adsorbility[2,3] at lower acidities. Perchloric acid exhibited similar trend[4]. Several mixed solvent systems were employed for its separations from many ions. It was observed in hydrochloric acid-alcohol (80-90%) system that it had the highest distribution coefficient[5,6], permitting separation of lithium from sodium[7]. Lithium was separated from various ions by the process of selective sorption from citrate[8] or oxalate[9] solutions.

However, systematic studies in mineral acid media are lacking. This paper presents systematic cation exchange chromatographic behaviour of lithium with mineral acids and their salts as the eluants. Various interesting separations of lithium from several other ions are also reported.

## Experimental

*Apparatus and reagents :* The ion-exchange column (1.4 × .0 cm) was similar to the one described earlier[10]. A digital pH meter (Type pH-822, ECIL Ltd., India) with glass and calomel reference electrodes and an automatic fraction collector (Emnvee Engg. Ltd., India) with 25 ml syphon was used. A digital flame photometer (Associated Instrument Manufacturing Ltd., India) was used.

A stock solution of lithium was prepared by dissolving 13.12 g of lithium sulphate (Reachim, U.S.S.R.) in 500 ml distilled water. It was standardized gravimetrically[11] and was found to contain 5 mg/ml of lithium.

Dowex 50W-X8 (50-100 mesh), H^{+} form, (Dow Chemical Co., U.S.A.) was used.

Lithium (5 mg) was sorbed on the column from an aliquot solution. After washing the column with 50 ml of distilled water, lithium was eluted with various eluants at a flow rate of 1 ml/min (Table 1). The effluent lot was collected in ten fractions each of 25 ml. Lithium from each fraction was determined flame photometrically. With mineral acids as the eluants, the effluent was evaporated to dryness before the flame photometric determination, however, when salts were used as the eluants it was not necessary to evaporate them to dryness. In such case lithium from the effluent lot was determined flame photometrically by standard addition method[12].

## Results and Discussion

The elution constant (E) and volume and weight distribution coefficients ($D_v$ and $D_w$) were evaluated from peak elution volume ($V_{max}$) as described earlier[13].

On the basis of elution constant (E), selectivity scale for eluants was,

$$HCl \geqslant HNO_3 \geqslant H_2SO_4 \rangle NH_4Cl \geqslant NaCl \rangle NH_4Br \rangle$$
$$\rangle NH_4I \rangle NH_4NO_3 \rangle CH_3COONH_4$$

When organic acids were tested as eluants, it was observed that citric and oxalic acid in any concentration proved to be poor eluants. Hydrochloric acid was most suitable eluant for routine work due to its small peak elution volume. Further, it was very easy to evaporate hydrochloric acid to dryness before flame photometric determination of lithium.

*Ion-Exchange separation :* These separations are based on the exploitation of the difference in the exchange potentials of different ions with respect to the resin. Certain ions which were capable of forming anionic complexes ; passed through the column unabsorbed leaving behind lithium on the column, which was later eluted with suitable eluant. In few instances, lithium along with other ions was sorbed on the column and later eluted with specific eluant (Table 2).

*Selective elution of lithium :* Lithium was taken up weakly by the resin in comparison with few elements and hence it was eluted first, while strongly adsorbed ions were eluted later with suitable eluants. Thus, lithium was separated from

TABLE 1—CATION EXCHANGE BEHAVIOUR OF LITHIUM ON DOWEX 50W-X8

| Eluant | Concen-tration (M) | Peak elution volume Vmax, ml | Total elution volume Vt, ml | Lithium recovery (%) | Elution constant (E) | Volume distribu-tion coefficient (Dv) | Weight distribu-tion coefficient (Dw) |
|---|---|---|---|---|---|---|---|
| HCl | 0.25 | 150 | 250 | 96.8 | 0.23 | 4.30 | 3.31 |
| | 0.5 | 100 | 225 | 98.2 | 0.37 | 2.68 | 2.06 |
| | 1.0 | 75 | 200 | 99.8 | 0.54 | 1.86 | 1.43 |
| | 2.0 | 50 | 175 | 100.1 | 0.95 | 1.05 | 0.81 |
| HNO₃ | 0.25 | 150 | 300 | 99.8 | 0.23 | 4.30 | 3.31 |
| | 0.5 | 100 | 225 | 99.6 | 0.37 | 2.68 | 2.06 |
| | 1.0 | 75 | 200 | 101.0 | 0.54 | 1.86 | 1.43 |
| | 2.0 | 50 | 200 | 100.2 | 0.95 | 1.05 | 0.81 |
| H₂SO₄ | 0.25 | 150 | 300 | 79.9 | 0.23 | 4.30 | 3.31 |
| | 0.5 | 75 | 2C0 | 96.8 | 0.54 | 1.86 | 1.43 |
| | 1.0 | 50 | 200 | 99.9 | 0.95 | 1.05 | 0.81 |
| | 2.0 | 50 | 175 | 99.1 | 0.95 | 1.05 | 0.81 |
| NaCl | 1.0 | 75 | 200 | 100.1 | 0.54 | 1.86 | 1.43 |
| NH₄Cl | 0.5 | 125 | 200 | 98.8 | 0.29 | 3.49 | 2.68 |
| | 1.0 | 75 | 175 | 99.2 | 0.54 | 1 86 | 1.43 |
| | 2.0 | 50 | 150 | 99.7 | 0.95 | 1.05 | 0 81 |
| NH₄Br | 0.5 | 100 | 225 | 99.7 | 0.37 | 2.68 | 2.06 |
| | 1.0 | 75 | 175 | 99.8 | 0.54 | 1.86 | 1.43 |
| | 2.0 | 50 | 175 | 99.9 | 0.95 | 1.05 | 0.81 |
| NH₄I | 0.5 | 100 | 200 | 98.6 | 0.37 | 2.68 | 2.06 |
| | 1.0 | 75 | 175 | 98.8 | 0.54 | 1.86 | 1.43 |
| | 2.0 | 50 | 150 | 100.2 | 0.95 | 1 05 | 0.81 |
| NH₄NO₃ | 0.5 | 100 | 200 | 96.8 | 0.27 | 2.68 | 2.06 |
| | 1.0 | 75 | 125 | 98.9 | 0.54 | 1.86 | 1.43 |
| | 2.0 | 50 | 125 | 97.9 | 0.95 | 1.05 | 0.81 |
| CH₃COONH₄ | 0 5 | 125 | 225 | 97.7 | 0.29 | 3.49 | 2.68 |
| | 1.0 | 75 | 200 | 99.8 | 0.54 | 1.86 | 1.43 |
| | 2.0 | 75 | 200 | 99.9 | 0.54 | 1.86 | 1.43 |

TABLE 2—SEPARATION OF LITHIUM FROM VARIOUS
OTHER ELEMENTS

| Foreign ions | Amount of foreign ion added, mg | Lithium taken mg | Lithium found mg | Recovery of lithium, (%) |
|---|---|---|---|---|
| Ca | 6.0 | 5.00 | 5.00 | 100.0 |
| Sr | 5.3 | 5.04 | 5.05 | 100.2 |
| Ba | 4.8 | 5.00 | 4.94 | 98.8 |
| Cr(III) | 6.2 | 5.00 | 4.89 | 97.8 |
| Mn(II) | 4.3 | 5.00 | 4.92 | 98.4 |
| Co(II) | 6.2 | 5.03 | 5.01 | 99.6 |
| Ni(II) | 5.3 | 5.04 | 5.05 | 100.2 |
| Al | 7.4 | 5.00 | 5.09 | 101.8 |
| Sc | 5.3 | 5.04 | 5.05 | 100.2 |
| Tl(I) | 8.2 | 5.04 | 5.05 | 100.2 |
| Be | 7.2 | 5.00 | 4.93 | 98.6 |
| Mg | 4.8 | 5.00 | 4.99 | 99.9 |
| Y | 5.0 | 5.00 | 4.98 | 99.6 |
| Ti(IV) | 4.9 | 5.00 | 4.96 | 99.2 |
| Zr | 4.7 | 5.C0 | 4.99 | 99.8 |
| Hf | 4.0 | 5.04 | 5.05 | 100.2 |
| Sb(III) | 5.0 | 5.00 | 4.90 | 98.0 |
| Na | 10.0 | 5.00 | 4.97 | 99.4 |
| K | 10.0 | 5.00 | 4.98 | 99.6 |
| Rb | 10.0 | 5.00 | 4.95 | 99.0 |
| Cs | 10.0 | 5.00 | 4.99 | 99.8 |
| Fe(III) | 8.3 | 5.00 | 4.98 | 99.6 |
| Cd | 9.8 | 5.00 | 4.92 | 98.4 |
| Hg(II) | 5.5 | 5.00 | 4.95 | 99.0 |
| In | 7.7 | 5.00 | 4.97 | 99.4 |
| Bi(III) | 7.6 | 5.00 | 4.99 | 99.8 |
| CrO₄²⁻ | 10.0 | 5.00 | 4.99 | 99.8 |
| TeO₃²⁻ | 8.8 | 5.00 | 4.99 | 99.3 |
| SeO₃²⁻ | 14.0 | 5.00 | 4.99 | 99.8 |
| AsO₃³⁻ | 6.0 | 5.00 | 4.99 | 99.8 |

alkaline earths by the process of gradient elution with $0.25M$ nitric acid followed by the elution of calcium, strontium or barium with $1M$ nitric acid.

Chromium(III), manganese(II), cobalt(II), nickel(II) and aluminium were separated from lithium by first eluting lithium with $0.5M$ hydrochloric acid followed by the elution of other ions with $2M$ hydrochloric acid.

Lithium was separated from scandium by gradient elution with $1M$ and $4M$ ammonium chloride respectively, and also from thallium(I) by gradient elution with $0.5M$ and $2M$ ammonium acetate respectively.

*Selective retention of lithium :* Lithium was retained strongly by the resin in comparison with few ions and hence could be eluted after the elution of weakly bound ions.

Thus, lithium was separated from beryllium, magnesium or yttrium by eluting them first with $0.1M$ hydrochloric acid ($0.5M$ ammonium acetate for yttrium) followed by the elution of lithium with $1M$ hydrochloric acid.

*Separation of anions and anionic complexes by the process of selective sorption :* Titanium, zirconium, hafnium(IV) and antimony(III) formed negatively charged citrato complexes with 5% citric acid at $pH$ 2.7. Under these conditions, lithium could not form any complex. Therefore on passing the mixture of these metals in the presence of citric acid at $pH$ 2.7, the negatively charged complexes passed through the column while lithium was retained on the column. It was latter eluted with $1M$ hydrochloric acid. It was possible to separate chromate, tellurite, selenites and arsenite by the process of selective sorption.

*The sequential separation of alkali metals :* Lithium could be separated from sodium, potassium, rubidium and cesium by taking the advantage of their varying adsorbability. Such variation originated from increasing ionic radii or decreasing radii of hydrated cationic species.

Lithium was eluted first with 225 ml of 0.20$M$ hydrochloric acid then sodium with 200 ml of the same eluant; further, potassium was eluted with 1$M$ hydrochloric acid in 40% ethanol and finally rubidium and cesium together with 2$M$ hydrochloric acid. It was not possible to separate rubidium from cesium on account of tailing effect.

*Separation of lithium in mixed solvent systems :* The adsorbability of lithium on cation exchange resin, showed substantial increase in the presence of organic solvents such as, methanol, ethanol, iso-propanol, acetone, dioxan and tetrahydrofuran[4-6]. On account of unusual rise in distribution coefficient, there was significant increase in the magnitude of the separation factor. Although, mixed solvent systems was used earlier, it was mainly used for its separation from alkali metals or alkaline earths. Hence new methods were developed for its separation from iron(III), cadmium, mercury(II) indium and bismuth(III) in mixed solvent systems[14].

On passing the mixture of lithium with these ions, first they were eluted with 0.5$M$ hydrochloric acid containing organic solvents like 80% acetone for iron(III) ; 60% iso-propanol for cadmium ; 40% methanol for mercury(II) ; 60% tetrahydrofuran for indium and 20% ethanol for bismuth(III). Lithium was eluted later with 1$M$ hydrochloric acid.

It was possible to separate lithium from foreign ions in the ratios exceeding 1 : 3. The volume of the eluant used in all separations was 200 ml. The separation of lithium from alkali and alkaline earths is significant as they are usually associated with each other. Similarly separation from aluminium, magnesium, cobalt, nickel and thallium is useful, as they are associated with it in several minerals.

The overall operation needs about 3 hr. The results are reproducible to ±1.2%.

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