Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Gaubert, E. , Barnier, H. , Nicod, L. , Favre-Reguillon, A. , Foos, J. , Guy, A. , Bardot, C. and Lemaire, M.(1997) 'Selective Cesium Removal from a Sodium Nitrate Aqueous Medium by Nanofiltration—Complexation', Separation Science and Technology, 32: 14, 2309 — 2320

To link to this Article: DOI: 10.1080/01496399708000770

URL: http://dx.doi.org/10.1080/01496399708000770

SEPARATION SCIENCE AND TECHNOLOGY, 32(14), pp. 2309–2320, 1997

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ABSTRACT

In aqueous medium, selective complexation increases the ionic separation by nanofiltration. Within the context of the nuclear effluent treatment, the nanofiltra-

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tion–complexation association is applied to sodium/cesium separation. Resorcinarene, a water-soluble ligand of cesium, is associated to the FILMTEC NF 70 membrane. Effects of pH, transmembrane pressure, ligand concentration, and ionic strength on salts retention and filtration fluxes are described. Finally, cesium complexation constants with resorcinarene are determined by using the nanofiltration–complexation process.

INTRODUCTION

Nuclear effluents usually contain traces of radioelements in a concentrated sodium salt medium. Vitrification allows the storage and the volume reduction of nuclear wastes. However, sodium salt excess is unfavorable for the vitrification and, consequently, sodium salt separation is necessary. Precipitation, solid–liquid, or liquid–liquid extraction can be used, but these processes involve other wastes production. Nanofiltration is a pressure-driven membrane process which produces very few additional waste. Located between ultrafiltration and reverse osmosis, the "cutoff" of nanofiltration membranes is in the range of 300 to 1000 $kg \cdot kmol^{-1}$ molecular weight (1, 2). Organic, mineral, or composite nanofiltration membranes exhibit pores which can be electrically charged, and ionic separations have been widely observed during the last decade (1–3). Moreover, to increase ionic separation, nanofiltration can be associated with a selective complexation step (4). In this way, retention of the target element is improved because the ligand does not pass through the membrane. A water-soluble ligand with a low molecular weight (about 500 $kg \cdot kmol^{-1}$) can be used for nanofiltration–complexation association, whereas microfiltration– or ultrafiltration–complexation systems requires larger ligands (5–10).

The aim of this study is to separate cesium from a sodium salt excess. To reach this goal, we experimented with a nanofiltration process with and without a complexation step. Resorcinarene **1**, presented in Fig. 2, was used as a water-soluble ligand of cesium.

EXPERIMENTAL

Membrane System

Figure 1 is a scheme of the nanofiltration loop. By totally recycling the permeate, the feed remains at constant composition during the experiments. Nanofiltration was carried out with the FILMTEC NF 70 (2514) spiral wound membrane (MWCO ≈ 300 $kg \cdot kmol^{-1}$). The membrane surface area was 0.5 m^2 and the water permeability was about 5 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$.

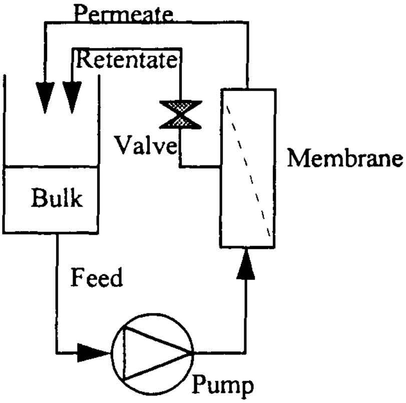

FIG. 1 Nanofiltration apparatus scheme.

Chemicals and Reagents

Although the synthetic model solutions are nonradioactive, they represent the nuclear effluent. They contain cesium traces (mmol·L^{-1}) in a sodium nitrate medium (mol·L^{-1}). Cesium and sodium concentrations were determined by atomic emission in a acetylene-air flame (Perkin Elmer 3110). Before pH ajustment with nitric acid and sodium hydroxide, the aqueous waste simulants were prepared by dissolution in distilled water:

Sodium nitrate 99% (Prolabo)
Cesium nitrate 99% (Aldrich)

Resorcinarene **1** was synthetized according to the procedure described by Högberg (11). This synthesis (yield 90%) led to a mixture (4/1) of **1**rccc and **1**rctt isomers (11) which are presented in Fig. 2. ^{1}H-NMR spectra were recorded at 200 MHz with a Brucker AC 200 spectrometer and with the solvent proton signal as the standard. ^{13}C-NMR spectra were recorded at 50 MHz with a Brucker AC 200 spectrometer and with the solvent carbon signal as the standard.

^{1}H NMR: 1.6–1.7 (d, CH_3, J = 7.3 Hz); 4.4–4.5 (q, CH, J = 7.3 Hz); 5.9 (s, 1H, $H_{arom.}$ *ortho*); 7.2 (s, 1H, $H_{arom.}$ *meta*).

^{13}C NMR (D_2O/NaOD 0.5 M): 155.86 (HO—$C_{arom.}$); 127.06 (C—$C_{arom.}$); 121.37 (H—$C_{arom.}$ *ortho*); 106.62 (H—$C_{arom.}$ *meta*); 29.12 (CH); 19.08 (CH_3).

Retentions (R_i) and transmission coefficients (T_i) are calculated as follows:

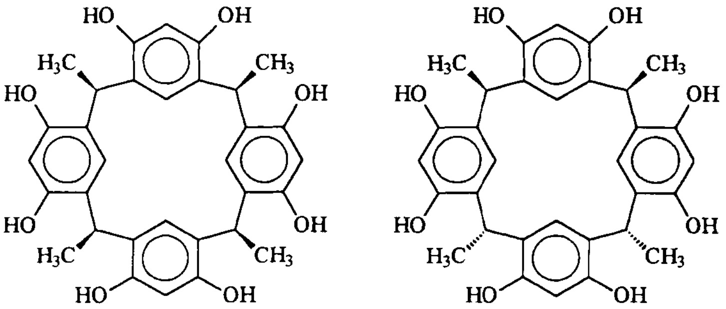

FIG. 2 Resorcinarene 1 isomers.

$$R_i = ((C_{ir} - C_{ip})/C_{ir})\cdot 100$$

$$T_i = 100 - R_i$$

where C_{ir} = i solute concentration in the retentate
C_{ip} = i solute concentration in the permeate

RESULTS AND DISCUSSION

Retentate pH Effect on Salts Retention without Ligand

Retentate pH effect on salts retention and filtration fluxes are presented in Fig. 3. Whatever the retentate pH, cesium retention is always lower or equal to sodium retention. However, note three pH areas:

From pH 3 to about 4: Salt retention decreases when the retentate pH increases, but cesium retention is always lower than sodium retention. In this case, Donnan exclusion is not involved because the excess sodium screens off the negative surface charges of the FILMTEC NF 70 membrane (12). Also, ionic mobility does not affect salt retention because the ionic strength is too high (13, 14). Ionic size is the main parameter controlling salts retention, which depends on the hydration enthalpy [$\Delta H°\,\mathrm{Na}^+ = -449\,\mathrm{kJ\cdot mol^{-1}}$; $\Delta H°\,\mathrm{Cs}^+ = -316\,\mathrm{kJ\cdot mol^{-1}}$ (15)].

From pH about 4 to 6: Cesium retention is lower than sodium retention but the two retentions increase with retentate pH. Salt retention is always controlled by ionic size.

From pH about 6 to 9: Cesium and sodium retentions are equal and increase with the retentate pH.

Because the chemical composition of the FILMTEC NF 70 membrane is unknown, these salts retention variations with retentate pH can not be

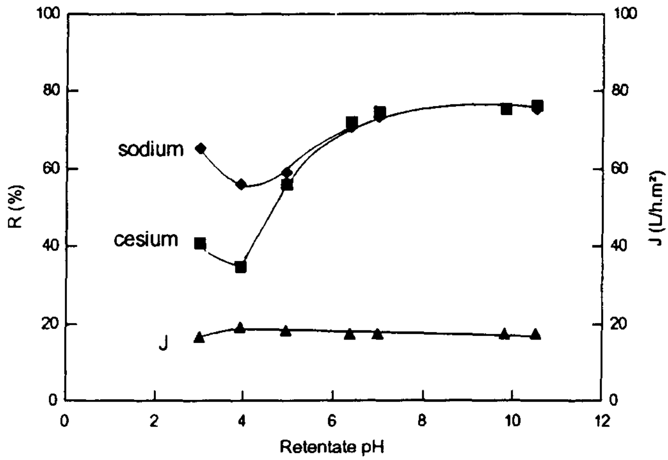

FIG. 3 Retentate pH effect on salts retention and filtration fluxes. $[Na^+] = 87\ mmol \cdot L^{-1}$, $[Cs^+] = 0.32\ mmol \cdot L^{-1}$, $\Delta P = 0.5$ MPa, $T = 303$ K.

explained. Filtration fluxes depend on the osmotic pressure difference between retentate and permeate, which is proportional to sodium retention.

The performance of the FILMTEC NF 70 membrane is insufficient to concentrate cesium traces in a sodium nitrate medium. In order to increase membrane selectivity, the nanofiltration–complexation association was experimented with. Cesium complexation was studied by using the resorcinarene **1** ligand.

Resorcinarene–FILMTEC NF 70 Membrane Association for the Sodium/Cesium Separation

Interest in calix[4]arene as a selective ligand for the removal of cesium from medium-level radioactive waste has increased (16). Resorcinarene **1** (11), synthetized from resorcinol and acetaldehyde, has been studied by numerous workers and has been found to lead to interesting host–guest complexes in solution (17, 18). However, the metal-complexing ability of resorcinarene **1** has not been reported previously.

Resorcinarenes are highly soluble in aqueous basic solution because of the deprotonation of the phenolic hydroxyl groups. However, in the case of resorcinarene **1**, four protons are much more acidic than the others: these protons reveal a pK_a value two units below the pK_a of resorcinol

($pK_{a_{(resorcinol)}} = 9.8$), whereas the remaining four cannot even be removed with a strong base like sodium methoxide (18).

The tetra-anion of resorcinarene **1** (Fig. 4) which exists in aqueous alkaline solution (19) may served as the anionic host molecule (L) in a cesium complex (Cs—L). The selective extraction of cesium may occur because of its dimensional matching to the cavity of resorcinarene **1** (20), cooperative cesium–arene interactions (16, 20), and the selectivity of phenolic groups for cesium (21).

Finally, resorcinarene **1** retention is expected to be high because its molecular weight (about 544 kg·kmol^{-1}) is larger than that of the FILMTEC NF 70 "cutoff" (about 300 kg·kmol^{-1}).

Resorcinarene Concentration and Salinity Effects on Salts Retention

The resorcinarene **1** concentration effect on salts retention and filtration fluxes is presented in Fig. 5 for two different ionic strengths. Different transmembrane pressures were applied in order to keep the filtration flux constant whatever the salinity.

Cesium retention increases with resorcinarene **1** concentration, but no significant consequence on sodium retention was noticed. In this way, sodium/cesium separation is improved. However, the ligand excess does not allow complete cesium complexation. To explain this partial complexation, some assumptions are suggested:

pH limits of the FILMTEC NF 70 utilization (3 < pH < 9) impose a nanofiltration pH too low for cesium complexation. It has been previously shown (22) that with resorcinol–formaldehyde resin the cesium

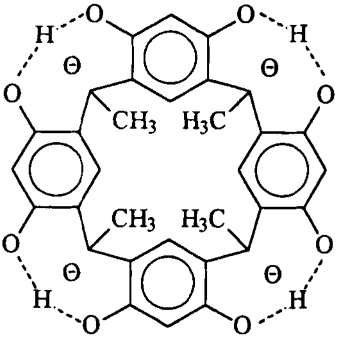

FIG. 4 Tetra-anion of resorcinarene **1** (L).

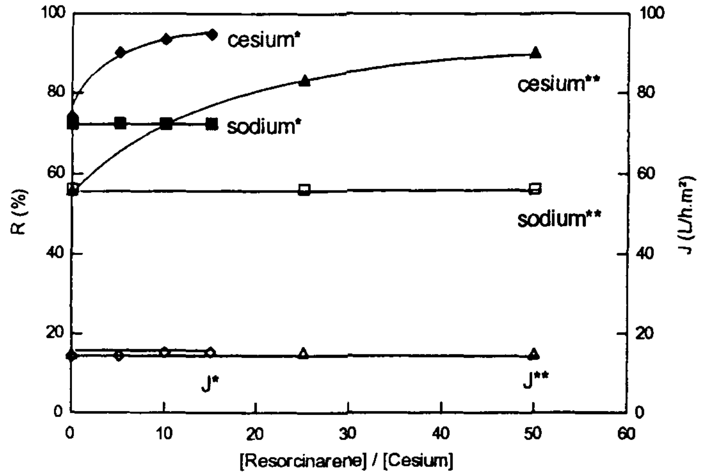

FIG. 5 Resorcinarene **1** concentration and salinity effects on salts retention and filtration fluxes. $[Cs^+] = 0.075$ mmol·L^{-1}, pH 9, $T = 298$ K. * $[Na^+] = 87$ mmol·L^{-1}, $\Delta P = 0.5$ MPa. ** $[Na^+] = 470$ mmol·L^{-1}, $\Delta P = 1.5$ MPa.

extraction increases with the pH, while that of sodium is independent of the solution basicity. The optimal pH is 14.

A competitive complexation between cesium and sodium can take place.

At high ionic strength, resorcinarene **1** conformation could be unfavorable for cesium complexation.

The constancy of filtration fluxes shows that membrane fouling does not occur at any ligand concentration.

By using these results, cesium complexation constants with resorcinarene **1** can be evaluated if:

Cesium hydroxide amounts are neglected.

Cesium–resorcinarene **1** complex (Cs—L) is totally rejected.

Cesium is complexed by the tetra-anion of resorcinarene **1** (L) in a ratio of 1 to 1 according to the following reaction scheme:

$$\mathrm{Cs} + \mathrm{L} \xleftrightarrow{\beta} \mathrm{Cs{-}L}$$

The cesium complexation constant, β(Cs—L), is given by

$$\beta(\mathrm{Cs{-}L}) = \frac{[\mathrm{Cs{-}L}]}{[\mathrm{Cs}]\cdot[\mathrm{L}]} \tag{1}$$

The concentration of uncomplexed cesium, [Cs], is expressed by

$$[\mathrm{Cs}] = [\mathrm{Cs}]_i \frac{T_{(\mathrm{Cs})}}{T^i_{(\mathrm{Cs})}} \tag{2}$$

where $[\mathrm{Cs}]_i$ is the initial cesium concentration, $T^i_{(\mathrm{Cs})}$ is the transmission coefficient for cesium without ligand, and $T_{(\mathrm{Cs})}$ is the transmission coefficient for cesium with ligand. The complex concentration, [Cs—L], is given by

$$[\mathrm{Cs{-}L}] = [\mathrm{Cs}]_i - [\mathrm{Cs}] \tag{3}$$

From Eqs. (2) and (3) we obtain

$$[\mathrm{Cs{-}L}] = [\mathrm{Cs}]_i \left(1 - \frac{T_{(\mathrm{Cs})}}{T^i_{(\mathrm{Cs})}}\right) \tag{4}$$

The free ligand concentration, [L], is given by

$$[\mathrm{L}] = [\mathrm{L}]_i - [\mathrm{Cs{-}L}] \tag{5}$$

where $[\mathrm{L}]_i$ is the initial ligand concentration.

From Eqs. (4) and (5) we obtain

$$[\mathrm{L}] = [\mathrm{L}]_i - [\mathrm{Cs}]_i \left(1 - \frac{T_{(\mathrm{Cs})}}{T^i_{(\mathrm{Cs})}}\right) \tag{6}$$

Substitution of Eqs. (2), (4), and (6) into Eq. (1) gives Eq. (7) in which every term is known:

$$\beta(\mathrm{Cs{-}L}) = \frac{1 - y}{y[\mathrm{L}]_i(1 - x(1 - y))} \tag{7}$$

with $x = [\mathrm{Cs}]_i/[\mathrm{L}]_i$ and $y = T_{(\mathrm{Cs})}/T^i_{(\mathrm{Cs})}$.

If transmembrane pressure effect is neglected, complexation constants (Table 1) clearly decrease when sodium concentration increases. To generalize, complexation constants depend on ionic strength. Variations of the resorcinarene **1** conformation with salinity and the competitive complexation between sodium and cesium can explain these results.

Transmembrane Pressure and Salinity Effects on Salts Retention

We experimented with model solutions contain resorcinarene 1 and cesium traces in two different excesses of sodium nitrate. Transmembrane pressure and salinity effects on salts retention and filtration fluxes are presented in Figs. 6 and 7.

TABLE 1
Ionic Strength Effect on Cesium Complexation Constants

$[NaNO_3]$ (mmol·L^{-1})	$[L]_i$ (mmol·L^{-1})	Log β(Cs—L)
87	0.47	(8.2 ± 0.5)[a]
87	0.94	(8.1 ± 0.5)[a]
87	1.40	(8.0 ± 0.5)[a]
470	1.90	(6.8 ± 0.5)[b]
470	3.80	(6.9 ± 0.5)[b]

[a] $[Cs^+]$ = 0.065 mmol·L^{-1}, ΔP = 0.5 MPa, pH = 9, T = 298 K.

[b] $[Cs^+]$ = 0.083 mmol·L^{-1}, ΔP = 1.5 MPa, pH = 9, T = 298 K.

First, filtration fluxes decline when salinity increases because the osmotic pressure difference (between retentate and permeate) and viscosity increase. Second, salts retention declines when the salinity increases. Some assumptions can explain this result:

An excess of sodium counter ion screens off the negative surface charges of the membrane. Consequently, nitrate co-ions pass through the mem-

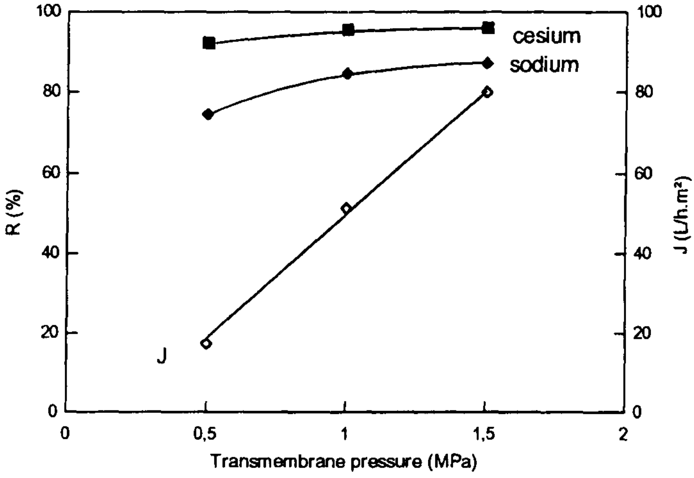

FIG. 6 Transmembrane pressure and salinity effects on salts retention and filtration fluxes. [Resorcinarene]/$[Cs^+]$ = 12.5, $[Cs^+]$ = 0.075 mmol·L^{-1}, $[Na^+]$ = 87 mmol·L^{-1}, pH 9, T = 303 K.

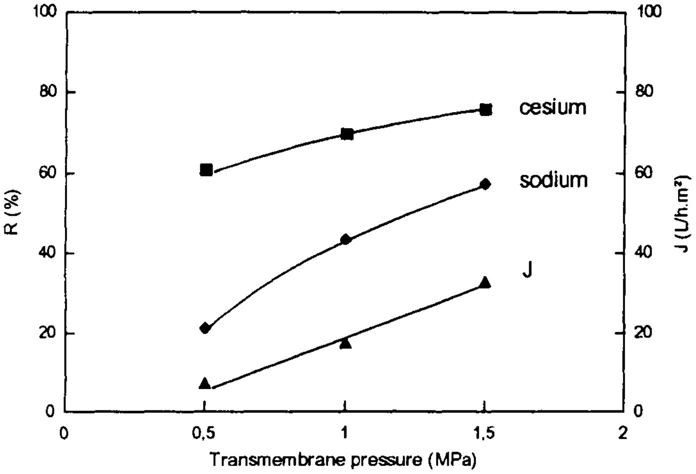

FIG. 7 Transmembrane pressure and salinity effects on salts retention and filtration fluxes. [Resorcinarene]/[Cs^+] = 12.5, [Cs^+] = 0.075 mmol·L^{-1}, [Na^+] = 470 mmol·L^{-1}, pH 9, T = 303 K.

brane without being rejected by the fixed negative charges (23, 24). Nitrates migrate with cesium and sodium counter ions to maintain electroneutrality. However, in our case this effect doesn't prevail because charge exclusion has been neglected.

The degree of ionic hydration declines when the ionic strength increases. Competitive complexation between cesium and sodium can occur.

The resorcinarene **1** conformation, which depends on the ionic strength, becomes unfavorable for cesium complexation at high salinity.

Although all these effects come together, the two last seem to predominate. New studies are now underway to confirm the predominant effects on salts retention.

As expected, filtration fluxes depend directly on the transmembrane pressure. Finally, salts retention increases with transmembrane pressure. Transmembrane pressure favors solvent flux through the membrane without any effect on solute fluxes, and consequently the solute concentration in the permeate declines. Nevertheless, this phenomenon is limited by a simultaneous rise of polarization concentration and diffusion. It is noted that cesium, which is mainly complexed with resorcinarene **1**, seems to be less sensitive to the transmembrane pressure effect.

CONCLUSION

In alkaline medium, resorcinarene **1** is a cesium-selective ligand. In the presence of more than 1300 and 5600 equivalents of sodium, the cesium complexation constants (log β) with resorcinarene **1** are 8.1 and 6.9, respectively. In association with nanofiltration, this ligand improves sodium/cesium separation by the FILMTEC NF 70 membrane. To reach higher sodium/cesium separation, a multistage nanofiltration–complexation process can be carried out. However, selective complexation of cesium is penalized by a sodium salt excess. Within the context of the nanofiltration–complexation association, studies of resorcinarene **1** will continue because this ligand can be easily extracted from the effluent. Resorcinarene **1** precipitates in acid medium, and it can be reused if it is removed by filtration.

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Received by editor April 16, 1996
Revision received January 1997