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Cs^+/Na^+ Separation by Nanofiltration–Complexation with Resorcinarene

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ABSTRACT

Cesium-137 is considered as one of the most dangerous radioactive materials that can be very easy move into the environment and contaminate it. This study aims to determine the optimum conditions for cesium/sodium separation by nanofiltration (NF)–complexation on Nanomax 50 membrane with resorcinarene as the complexing agent. Protonation constants of resorcinarene were determined by potentiometric titration in 0.1 mol/L $NaNO_3$ at 25°C ($\log K_{H1} = 9.24 \pm 0.06$; $\log K_{H2} = 10.21 \pm 0.03$; $\log K_{H3} = 8.59 \pm 0.07$; $\log K_{H4} = 7.85 \pm 0.08$). The apparent formation constants of the Cs^+–resorcinarene ($\log K_{CsL}$) were determined by UV spectrophotometry to evaluate the selectivity of resorcinarene toward cesium complex formation as a function of the pH.

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Parameters such as the pH, [resorcinarene]/[Cs^+] ratio were studied to reach 80% of cesium rejection in 3 mol/L of $NaNO_3$. The stability of resorcinarene was studied as a function of the pH and the concentration of $NaNO_3$ by ^1H and ^{13}C NMR studies in D_2O. Resorcinarene stability up to 30 days in $[NaNO_3] = 2\,mol/L$ at pH 9 was determined, although at pH 12 and with the same sodium concentration, resorcinarene stability was 5 days. Finally, the conditions to reach 80% of cesium rejection in the presence of 2×10^4 fold of sodium were found at pH 10 with [resorcinarene]/[Cs^+] ratio of 25 or at pH 11 with [resorcinarene]/[Cs^+] ratio of 20.

Key Words: Nanofiltration; Complexation; Resorcinarene; Cesium.

INTRODUCTION

The radio elements contained in the effluents resulting from the cleaning or the decontamination of the nuclear installations must be treated before storage. These contaminated effluents contain strong sodium salt concentrations ($[NaNO_3] = 255\,g/L = 3\,mol/L$) along with radio element traces, such as ^{137}Cs, which should be concentrated to minimize the volume of waste. Separating traces of cesium from aqueous medium containing large sodium amounts is a difficult problem because cesium and sodium ions have a similar behavior in aqueous medium. Among the different techniques of cesium separation, such as liquid–liquid[1] or solid–liquid[2] extractions, the nanofiltration (NF)–complexation process represents a good alternative because it generates only wastewater without phase shift nor use of solvent.

Tangential membrane filtration is one of the most important developments in process engineering and environmental care. Among them, NF is a pressure membrane process with molecular weight cutoff (MWCO) between reverse osmosis (RO) and ultrafiltration (UF). The NF-organic membranes are ideally suited for rejecting organics with molecular weights$>$200 Da and multivalent ions.[3] Because of these characteristics, the NF technique shows a great potential for the separation of ions in aqueous phase. These properties allow the separation of different ion valences, but this selectivity is not generally ensured for the separation of ions with the same valences. This can be improved by associating the NF process with a preliminary selective complexation step of the target ions with ligands of molecular weight higher than the MWCO of the membranes.[4,5] Thus, the resulting complexes are retained by the membrane, whereas the noncomplexed ions pass through it. It is this principle of NF–complexation, which is applied throughout this study. Cesium/sodium separation by NF–complexation requires the use of water-soluble ligands selective for cesium. Among them, calixarenes such as tetrahydroxy-calix[4]arene-*bis*-crown[6] or 2,8,14,20-tetra(methyl) calix-[4]resorcinarene[7] (resorcinarene) are soluble in basic aqueous medium. With a great stability in strongly saline basic medium, calixarenes showed a better selectivity toward cesium than the resorcinarenes.[8,9] However multistep synthesis of calixarenes[6] and their solubility at $pH > 12$ limit their used with NF-organic membranes. The solubility of resorcinarene from $pH > 9$ and its one-step synthesis[10] prompt us to further study the resorcinarene.

This study provides useful information for choosing the optimal conditions to separate traces of cesium contained in high concentration sodium salt media by NF–complexation. Thus, the influence of pH,[11] $[\text{resorcinarene}]/[Cs^+]$[12] ratio were optimized to reach 80% of cesium rejection with 2×10^4 fold excess of sodium.

EXPERIMENTAL SECTION

Equipment

Experiments have been performed with Osmonics Sepa CF lab-scale membrane cell and a schematic flow diagram of the lab-scale membrane system is presented in Fig. 1. The membrane cell consists of two elements (cell body in polypropylene and cell holder in aluminum). For this membrane cell, the maximum operating temperature reaches 80°C and the maximum operating pressure reaches 7 bars. The feed stream is pumped from the feed tank to the cell body. The solution flows tangentially across the membrane surface. A heat exchanger allows to control the temperature during filtration experiments. Hydraulic parameters were monitored by using pressure gauges and flowmeters. The pH was measured with a combined pH electrode by using a KS120 (Radiometer Analytical) glass electrode saturated with a $KCl + AgCl$ solution.

For the characterization of the rejection coefficient of the membrane, the feed is kept at a constant composition during the experiments by totally recycling the permeate and the feed.

The rejection ($R\%$) of a substance i was calculated as follows: $R_i = 100 \times (1 - C_{ip}/C_{if})$, where C_{if} is the concentration of i in the feed and C_{ip} is the concentration of i in the permeate.

Membrane

The commercial membrane Nanomax 50 (Millipore) is a flat membrane constituted of polyamide layers, which were characterized previously.[13]

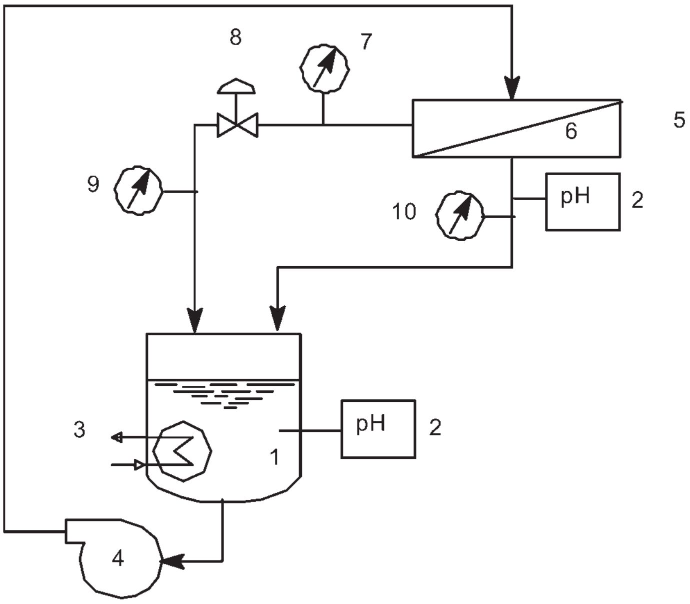

Figure 1. Schematic flow diagram of the lab-scale membrane system. 1, feed tank; 2, pH meter; 3, heat exchanger; 4, pump; 5, cell body; 6, membrane; 7, feed pressure gauge; 8, feed flow control valve; 9, feed flux meter; and 10, permeate flux meter.

The membrane area is of 155 cm^2 and the MWCO is 300 Da.[13] NF-organic membranes are used in a pH range between 2 and 12; otherwise, the membrane is damaged and its separation capacities decrease.[14] Before starting experiments, the membrane is conditioned by permeating distilled water at experimentation pH to reach the maximum permeability coefficient of the membrane.[15]

NF Test Procedure

Deionized water was used for the preparation of all solutions and for membrane performance experiments. An aqueous solution containing 0.11 mmol/L of cesium ($CsNO_3$ 99.99%, Aldrich) and 0.47 mol/L of sodium ($NaNO_3$ 99%, Aldrich) was filtered on an NF-membrane. NF tests were conducted by using a transmembrane pressure of 4 bars and a temperature of 20°C. Different known amounts of resorcinarene were progressively added to the solution containing 0.47 mol/L of $NaNO_3$ for different pH values, ranging between 9 and 12, and samples of permeate and feed were taken 45 min after each addition of ligand and each stage of pH. The pH values were adjusted with concentrated HNO_3 and NaOH.

In a second experiment, a solution containing 0.11 mmol/L of cesium and a fixed [resorcinarene]/[cesium] molar ratio, known amounts of sodium were progressively added for different pH values, ranging from 9 to 12. The resulting solution was filtered on a NF-membrane and the rejection ($R\%$) was determined. For each sample, the permeate flow is measured through a flowmeter. Each experiment was repeated three times to improve the reliability of the results.

Analytical Methods

The cesium concentration was determined by atomic absorption spectroscopy (AAS) in an air–acetylene flame (apparatus: PU 9100X Philips atomic absorption spectrometer). Each result must be assumed to have a 5% standard deviation due to uncertainty on the measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer, and δ values are given in ppm. Mass spectra were carried out by electrospray negative mode (ESIMS neg.) and were carried out on a Thermo Finnigan LCQ-Advantage. HP 8453 UV spectrophotometer was used for the measurement of the resorcinarene rejection and determination of Cs^+–resorcinarene complex formation constants according to the pH.

Protonation Constants

All solutions were prepared by using deionized water that was further purified by passing through a Millipore Alpha-Q RO cartridge system (resistivity 18.2 MΩ cm), and they were stored under purified argon to prevent absorption of oxygen and carbon dioxide. Carbonate free 0.1 M KOH was prepared from Merck concentrate (Titrisol) and was standardized by titrating potassium hydrogen phthalate (Aldrich). Solutions of 0.1 M HNO_3 were similarly prepared and were standardized by titrating TRIS buffer (Aldrich). Protonation constants were determined by pH-metric measurements by using a combined glass electrode (Metrohm). The calibration was carried out in a 100 mL glass-jacketed titration cell contained 0.1×10^{-3} mol/L of resorcinarene maintained under argon atmosphere at constant ionic strength ($I = 0.100$ $NaNO_3$) and temperature ($25.0 \pm 0.1°C$).[16] All titrations were performed by using a 716 DMS Titrino (Metrohm) equipped with a piston burette of 10 mL (addition volumes 20 μL) and controlled with the TiNet 2.4 software

(Metrohm) on a PC computer. The titration was performed over the pH range of 5.0–11.8, and the number of titration points used to calculate the protonation constants of resorcinarene were 150–200.

Before each titration, the electrode system was calibrated in hydrogen ion concentration units by titrating 4.00 mL of standardized HNO_3 diluted in 100 mL of 0.100 M $NaNO_3$ with standardized KOH.[17] The calibration data composed of pH values between 1.86 and 2.65 and 10.97 and 11.89 were processed by nonlinear least-squares minimization procedures available in Microsoft Excel to calculate the standard cell potential (E_o), the Nernst slope (S), together with the correction terms accounting for the changes in liquid junction potential in strongly acid (J_a) and alkaline (J_b) media. The sum of the unweighted square residuals on the observed emf readings (E_{mes}) is minimized according to the modified Nernst equation:

$$E_{mes} = E_o + S\log[H^+] + J_a[H^+] + J_b K_w [H^+]^{-1}$$

The base-concentration factor (γ) was also allowed to refine, whereas the ionic product of water was fixed ($pK_w = 13.78$). Calibration data were rejected when the standard deviation of the residuals exceeded 0.12 mV. The emf readings recorded for the subsequent titration were converted with the help of a Microsoft Excel spreadsheet into pH values by iterative solving of the equation:

$$pH = \frac{(E_o - E_{mes} + J_a[H^+] + J_b K_w [H^+]^{-1})}{S}$$

The protonation constants were refined by the weighted nonlinear least-squares program HYPERQUAD.[18] In the final refined step, the total amounts of titrated ligand and initially added acid were also allowed to vary. The $\log K_H$ values reported represent the average of three independent experiments.

Complexation Constants

The apparent formation constants of the Cs^+–resorcinarene ($\log K_{CsL}$) were determined by UV analysis for different pH values between 9 and 12. The resorcinarene (5×10^{-5} mol/L) was dissolved in an aqueous $NaNO_3$ solution (0.1 mol/L, 250 mL) at fixed pH. A progressive addition (50 μL) of a $CsNO_3$ solution (0.25 mol/L) leads a change in the resorcinarene UV absorption spectrum. The spectrum of the resorcinarene was recorded 50 min after each addition of cesium. We used the Foster–Hammick–Wardley method[8,19] to calculate $\log K_{CsL}$ from the absorption variations detected by UV spectrophotometry.

RESULTS AND DISCUSSION

Protonation Constants

The $\log K_{Hi}$ values of resorcinarene (L) in water were determined by pH-metric titration. Resorcinarene has eight acidity centers, but only four protonation constants can be determined by potentiometric titration in the range of pH 5.0–11.8. The remaining proton association reactions and constants can be represented by the following equations:

$$H_{4+i-1}L^{(4+i+1)-} + H^+ \rightleftarrows H_{4+i}L^{(4-i)-}$$

$$K_{H_i} = \frac{[H_{4+i}L^{(4-i)-}]}{[H^+][H_{4+i-1}L^{(4-i+1)-}]} \quad \text{for } 1 \leq i \leq 4$$

By continuing the substitution, an arbitrary resorcinarene species, $(H_{4+i}L^{(4-i)-})$, can be expressed in terms of equilibrium constants, free resorcinarene concentration and pH:

$$[H_{4+i}L^{(4-i)-}] = \left(\prod_{i=1}^{4} K_{H_i}\right)[H^+]^i[H_4L^{4-}] \tag{1}$$

$$[H_4L^{4-}] = \frac{L_0}{1 + \sum_{i=1}^{4}\left(\prod_{j=1}^{i} K_{H_j}\right)[H^+]^i} \tag{2}$$

with L_0, initial concentration.

The refined protonation constants values are presented in Table 1.

It was noticed that the resorcinol has two protonation constants ($\log K_{H1} = 11.06$ and $\log K_{H2} = 9.30$).[20] The observed modification puts in evidence the interactions between the OH groups. The relative proportions of each ionic species could then be deduced from each of the terms in

Table 1. Protonation constants of resorcinarene calculated by potentiometric titration in 0.1 mol/L $NaNO_3$ at 25°C.

$\log K_{H1}$	$\log K_{H2}$	$\log K_{H3}$	$\log K_{H4}$
9.24 ± 0.06	10.21 ± 0.03	8.59 ± 0.07	7.85 ± 0.08

Eqs. (1) and (2). Fractions of each ionic species of resorcinarene at a range of pH values from 5 to 12 are given in Fig. 2. Let us notice that the second protonation constant (log K_{H2}) is higher by 0.97 log K than the first protonation constant (log K_{H1}). This situation is very unusual, because the second stepwise protonation constant does not generally exceed the first one. This particularity can be ascribed to the higher stabilization of the tetra oxyanion by the formation of four hydrogen bonding reducing the basicity of the first protonation constant.[21]

From pH 11 to 12, only tetra anions are present in solution. At pH 10, three species are in equilibrium. The majority species is H_4L^{4-} with 70% of the total composition, whereas H_5L^{3-} and H_6L^{2-} represent 10% and 20%, respectively. Finally, at pH 9, five species are in equilibrium. Three are in minority each with 3% (H_8L, H_5L^{3-}, and H_4L^{4-}), but the fraction of H_7L^- is 21% and the majority fraction of H_6L^{2-} is 70%.

The UV spectrum (Fig. 3) of the resorcinarene according to the pH confirms the following results. Indeed, the hyperchromic effect appeared with the increasing of the pH solution from 9 to 10.5, without an isosbestic point. Consequently, more than two different forms of the resorcinarene between pH 9 and 10.5 are in equilibrium, which is in accordance with potentiometric data. Finally, no difference can be noticed between the UV spectra at pH 11.5

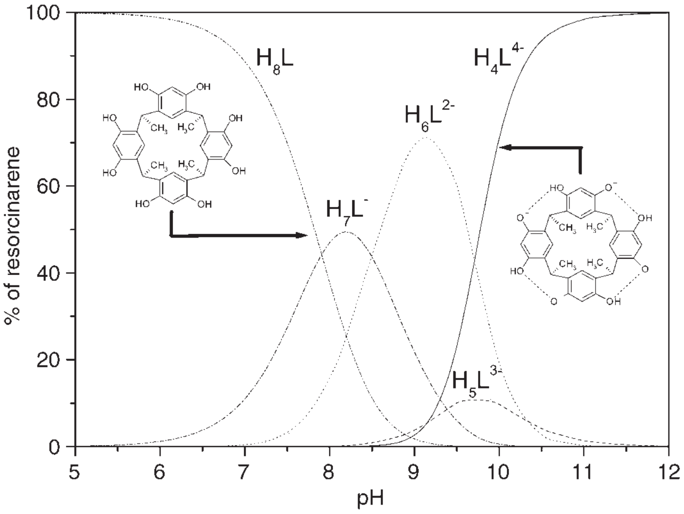

Figure 2. Plot of fraction of resorcinarene species in solution vs. pH for 0.1 mol/L $NaNO_3$.

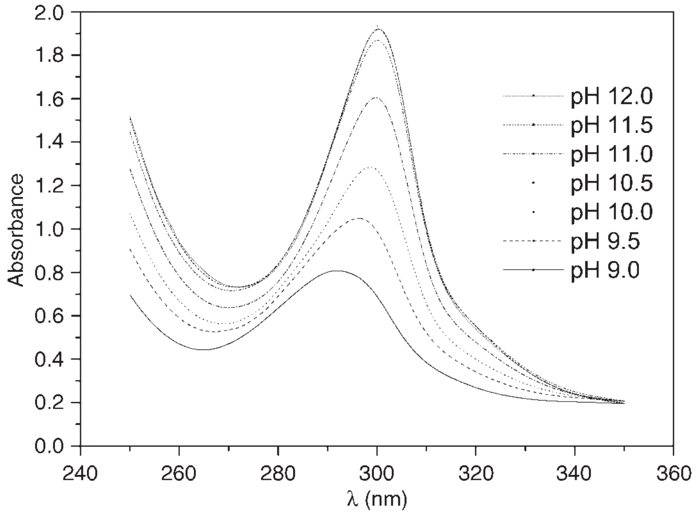

Figure 3. UV spectra of resorcinarene (1×10^{-3} mol/L) vs. pH.

and 12, because only one form of the resorcinarene could be present in solution in this range of pH (H_4L^{4-}).

Membrane Characterization

After the conditioning step, deionized permeate water flow at pH 5.8 was measured at different transmembrane pressures to determinate the pure water permeation fluxes $J_w = 6.5\,L/hr/m^2/bar$.

Permeate flux decreases with the increasing concentration of $NaNO_3$ (Fig. 4). At $[NaNO_3] = 0.47\,mol/L$, the flux is $5.7\,L/(hr\,m^2\,bar)$ whereas it is $2.7\,L/(hr\,m^2\,bar)$, at $[NaNO_3] = 3\,mol/L$. The increase of the solution viscosity by increase in $NaNO_3$ concentration is a factor that can reduce the permeate flux. Nevertheless, the permeate flux remains constant for all pH values. On the other hand, with the addition of resorcinarene (0.56 mmol/L), the permeate flux drops at a pH lower than 10 and remains nearly constant for higher pH values. At pH 9, the resorcinarene is less soluble and the fouling phenomena, corresponding to an adsorption[22] or a deposition[23] of the resorcinarene at the membrane surface, is one cause from this flux decline.[24,25] From pH 10, we did not observe any more particle deposition on the membrane. The permeate flux is recovered by increasing the pH from 9 to 12.

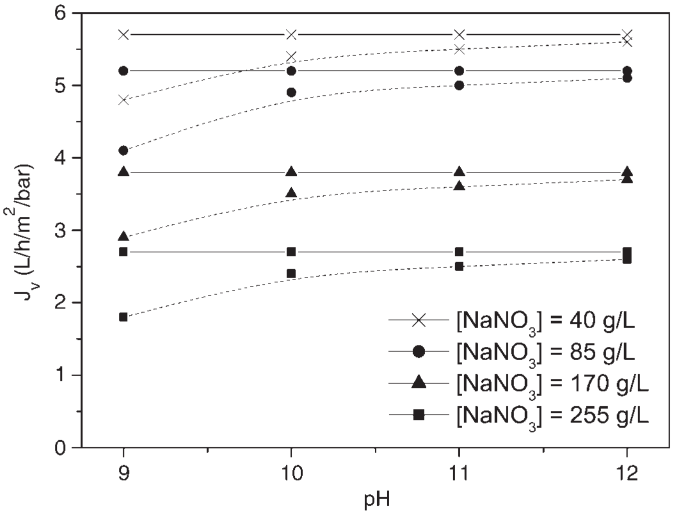

Figure 4. Plot of permeate flux (J_v) vs. pH in various salt concentration. Full lines correspond to the permeate flux with only $NaNO_3$; dot curves correspond to the permeate flux with $NaNO_3$ + resorcinarene ([resorcinarene] = 0.56 mmol/L; $T = 20°C$).

Without ligand, the membrane rejection of cesium and sodium reached 10% whatever the $NaNO_3$ concentration (Fig. 5), whereas the resorcinarene is entirely retained without cesium. Finally, the sodium concentration and pH do not have any effect on the initial rejection of cesium, sodium, and resorcinarene. The nitrate rejection could not determine precisely, but it should be equal the sodium retention to maintain electroneutrality.

Study of the Resorcinarene Stability in Aqueous Phase

The resorcinarene stability of resorcinarene was studied by ^1H and ^{13}C NMR in D_2O + NaOD with or without sodium, according to time and pH. In D_2O + NaOD solution, for pH 9–12, the boat isomer (all cis) configuration is exclusively present, confirmed by the presence of four resonance signals at 1.4 ppm (d, $J_1 = 7.4$ Hz, 3H), 4.42 ppm (q, $J = 7.28$ Hz, 1H), 5.77 ppm (s, 1H, ortho), and 6.99 ppm (s, 1H, meta) corresponding to the methyl, methylidene, and aromatics protons.

Without sodium, the resorcinarene is stable in aqueous solution from pH 9 to 12. In fact, no change was observed with the increasing of pH, even after more than 20 days. By increasing the salt concentration ([$NaNO_3$] =

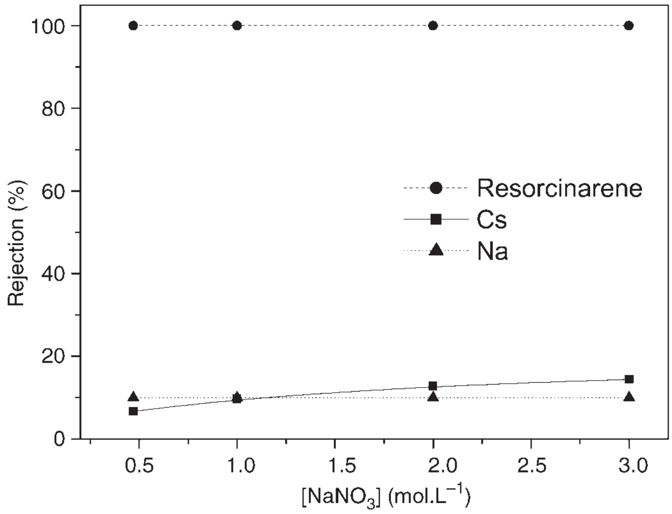

Figure 5. Plot of rejection of pure compound or ions as a function of the $NaNO_3$ concentration ([resorcinarene] $= 0.56\,mmol/L$; $[Cs^+] = 0.11\,mmol/L$; $pH = 11$; $\Delta P = 4\,bar$; $T = 20°C$).

2 mol/L = 170 g/L), the resorcinarene is stable for 10 days at pH 10 and 8 days at pH 11 (Fig. 6). But after 10 days at pH 11 in the presence of $NaNO_3$, ^1H NMR spectrum shows the degradation of the resorcinarene with the modification and the chemical shift of the triplet corresponding to the signal of resonance of CH of the ethylidenes bridges toward the weak fields. In very high salted solution ($[NaNO_3] = 3\,mol/L$) and whatever the pH, the resorcinarene is rapidly degraded less than 1 hr. The widening of the peaks of triplet is a consequence of the loss of the symmetry of the molecule. In the presence of sodium, the cleavage of aromatic ring of resorcinarene probably occurs involving a decrease in complexation of the cesium ion. In addition, the chemical shifts with $NaNO_3$ are superior to the chemical shifts without sodium salt. The variation of the chemical shifts $\Delta\delta = 0.12\,ppm$ is the result of the complexation of sodium by the resorcinarene in the presence of $NaNO_3$. ^1H and ^{13}C NMR demonstrate the stability of the ligand in highly salted media between pH 10 and 11. We have tried to determine the structure of the degraded product. NMR and mass spectroscopy of the precipitated and neutralized degradation product were not successful. During this study, we observed the ortho deuteration of the resorcinarene in D_2O at ambient temperature[26] (Fig. 7).

The proton deuteration exchange is observed in ^1H NMR by a decrease of the ortho proton signal resonance. This same exchange is also observed

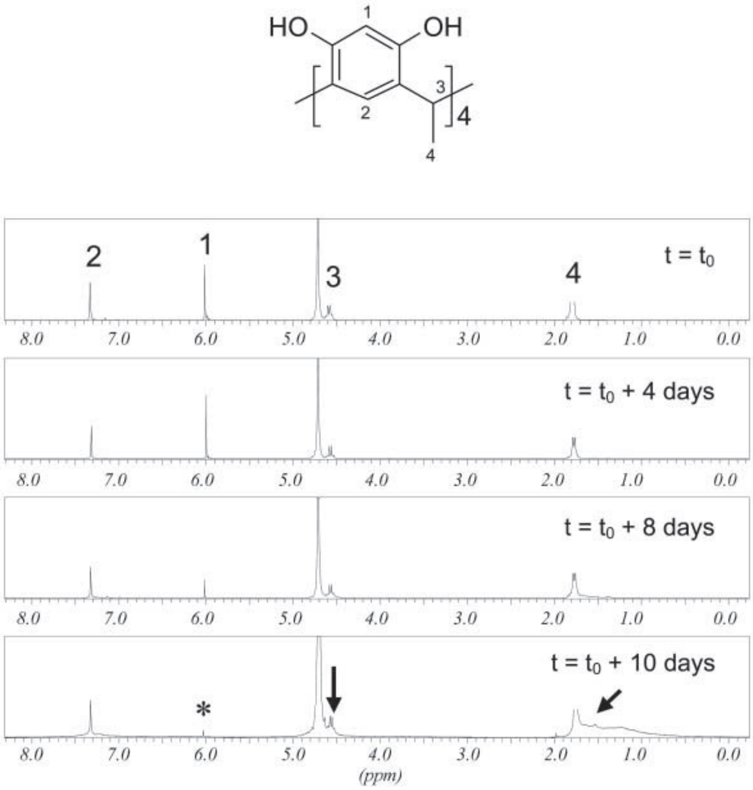

Figure 6. ^{1}H NMR spectra of resorcinarene according to time for [$NaNO_3$] = 2 M at pH 11 for resorcinarene = 50 mg/L (arrows indicate the widening of the signal of the CH_3 and CH groups of resorcinarene and * indicate the H–D exchange at carbon 1).

in ^{13}C NMR experiment by the disappearance of the Ar*C*H resonance signal, and the presence of a triplet (1 : 1 : 1) corresponding to the C–D coupling. H/D exchange involves a light isotopic effect on the chemical shift of ^{13}C–D of 0.5 ppm toward the high fields. In addition, the low intensity of the ^{13}C signal of the deuterated nuclei was due to the nuclear Overhauser effect, hence an increasing relaxation time justifying a considerable loss of the signal intensity (Fig. 8). It was found that the rate of the exchange was a function of the pH. The H/D exchange was twice faster at pH 10 than at pH 11, as determined by the kinetic evolution after 10 and 20 days, respectively. This deuteration has also been confirmed by mass spectroscopy (ESIMS neg.) with a signal at 547 uma corresponding to the $[M - H]^-$ tetra deuterated moiety, thus confirming the exhaustive tetra ortho deuteration of the resorcinarene.

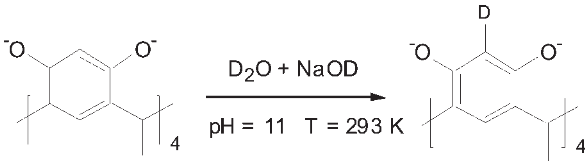

Figure 7. Scheme H/D exchange in ortho of the resorcinarene with D_2O in NaOD.

Separation Cesium/Sodium According to the pH and [$NaNO_3$]

Between pH 9 and 12, cesium rejection increases from 48% to 85%. Indeed, within this pH range, the resorcinarene can be found in different protonated species (Fig. 9). Above pH 11, the optimal cesium rejection was in accordance

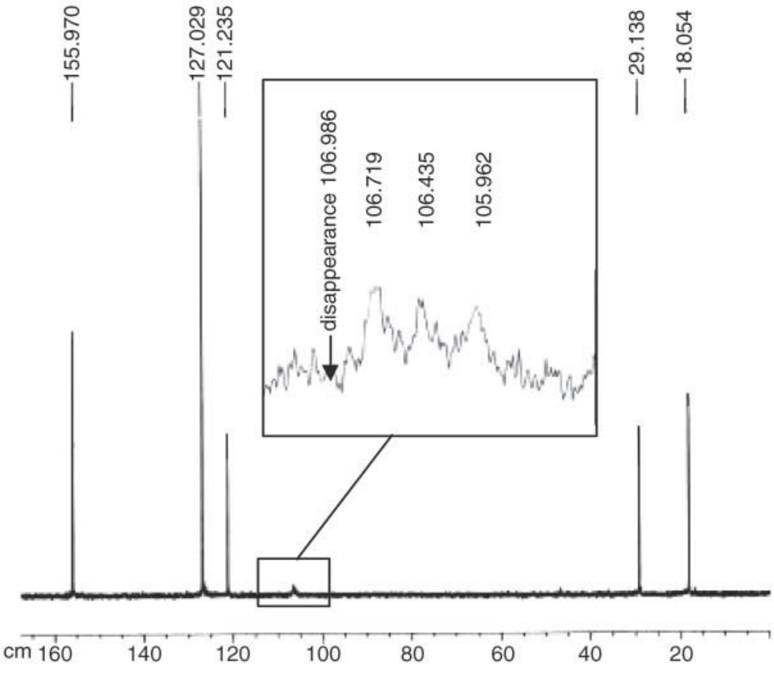

Figure 8. ^{13}C NMR spectrum of deuterated resorcinarene in D_2O at pH 10 for $t = t_0 + 10$ days, $T = 20°C$, [300 MHz with 9000 scans and m (resorcinarene) = 80 mg/L] and increase of triplet 1 : 1 : 1 corresponding to the $C-D_{ortho}$ coupling and disappearance of $C-H_{ortho}$ coupling.

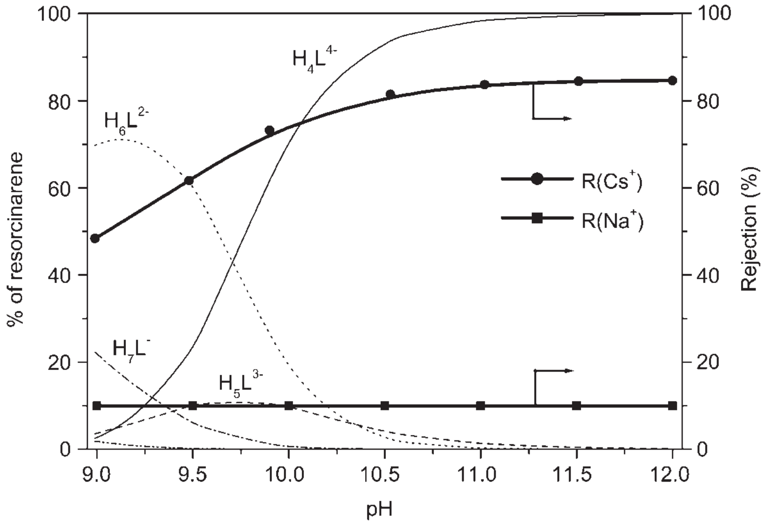

Figure 9. Plot of rejection of cesium vs. pH for 10 equivalents in resorcinarene ($[Cs^+] = 0.11\,mmol/L$; $[NaNO_3] = 0.1\,mol/L$; $\Delta P = 4\,bar$; $T = 20°C$) with fraction of resorcinarene species in solution.

with the presence of the tetraprotonated species (H_4L^{4-}), which stabilized the CsL complex. In addition, the cavity size of the macrocycle was in perfect adequation with the size of the nonhydrated cesium ion as expected by Lippmann et al.[27] Finally, phenolic nuclei exhibited high affinity for Cs^+ ions in alkaline media,[2b,28] and the partial deprotonated species preserved a conic conformation necessary for the stability of the cation in the cavity. On the other hand, at pH 9, several forms are in equilibrium between them without the tetraprotonated form but with a di-anion, which is in a majority. In these conditions, cesium rejection reached only 48%. The sodium rejection remains constant as a function of the pH, because the percentage of the Na–resorcinarene complex is low compared with the total concentration of Na.

These observations led us to study the Cs^+–resorcinarene complex formation constant (Table 2). The apparent formation constants $\log K_{CsL}$ were determined by UV spectrophotometry according to the pH and at $[NaNO_3] = 0.1\,mol/L$.[8]

The apparent formation constant of the Cs^+–resorcinarene complex increased by less than a factor of 2 from pH 9 to 12. Resorcinarene presented two potential complexation sites. The first one is pH dependent (phenolic groups) and the second stabilized Cs^+ by the Π-bonding interactions with the phenolic ring of resorcinarene.

Table 2. Determination of Cs^+–resorcinarene complex apparent formation constants according to the pH by UV spectrophotometry ([resorcinarene] = 5×10^{-5} mol/L; [$NaNO_3$] = 0.1 mol/L; $T = 20°C$).

$\log K'^{pH9}_{CsL}$	$\log K'^{pH10}_{CsL}$	$\log K'^{pH11}_{CsL}$	$\log K'^{pH12}_{CsL}$
5.81 ± 0.09	5.99 ± 0.08	6.12 ± 0.03	6.05 ± 0.06

Thus, we studied the influence of the pH and the [resorcinarene]/[Cs^+] ratio on cesium rejection. The rejection of cesium increases with the pH and with the concentration of resorcinarene (Fig. 10).

From pH 9 to 10, the rejection significantly increased of 21%. From pH 10 to 11, it only increased 6% for a [resorcinarene]/[Cs^+] ratio of 20. This increasing of cesium complex rejection maybe attributed to increasing the apparent formation constant of the Cs^+–resorcinarene complex as a function of the pH. Between pH 9 and 10, the increasing cesium complex rejection is also due to the increasing resorcinarene solubility, which is total from pH 9.5. Above pH 10, a [resorcinarene]/[Cs^+] ratio of 20 is required to have 80% of cesium rejection at [$NaNO_3$] = 0.47 mol/L. Under those conditions, at pH 9, total concentration of resorcinarene was lowered due to the fouling phenomena. Thus, to obtain 80% of rejection of Cs^+, threefold more resorcinarene

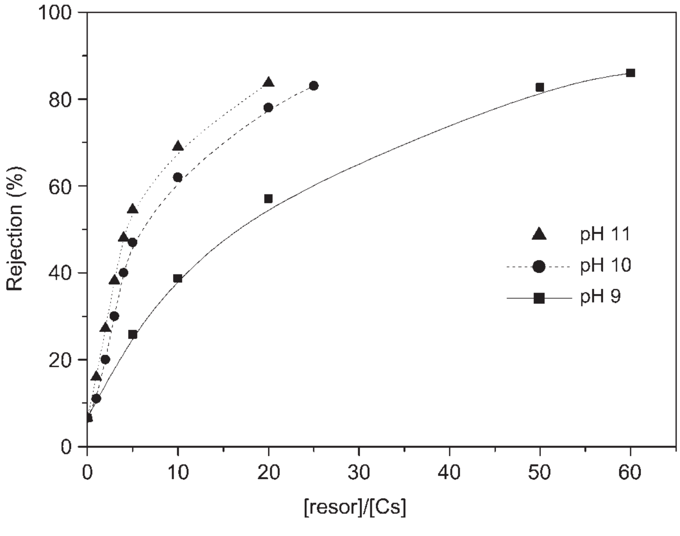

Figure 10. Plot of rejection of cesium vs. equivalent number of resorcinarene for pH 9–11 ([Cs^+] = 0.11 mmol/L; [$NaNO_3$] = 0.47 mol/L; $\Delta P = 4$ bar; $T = 20°C$).

concentration was needed at pH 9 than at pH 11. The concentration of resorcinarene to have cesium rejection of 80% at pH 9 is 6.76 mmol/L, whereas 2.81 and 2.24 mmol/L are necessary to obtain the same result at pH 10 or 11 (only 25% more at pH 10 than at pH 11).

Preliminary studies[8] showed that the rejection of the resorcinarene at pH 11 depended on the salinity of the medium with a decreasing rejection of the cation with an increase of [$NaNO_3$] (Fig. 11).

Between pH 10 and 12, the cesium rejection is closed although at pH 9 cesium rejection was 30% lower. The decrease in the rejection was related to a fast exchange between cesium and sodium inside the cavity of the macrocycle. When increasing sodium concentration, the apparent formation constant is shifted, leading to a decrease of cesium rejection.

CONCLUSION

In this study, the protonation constants of the resorcinarene were determined by potentiometric titration in a range of pH between 5.0 and 11.8 in 0.1 mol/L $NaNO_3$ at 25°C. The cesium–resorcinarene complex apparent formation constant was also determined by UV spectroscopy method in 0.1 mol/L $NaNO_3$ for different pH values ($9 \leq pH \leq 12$).

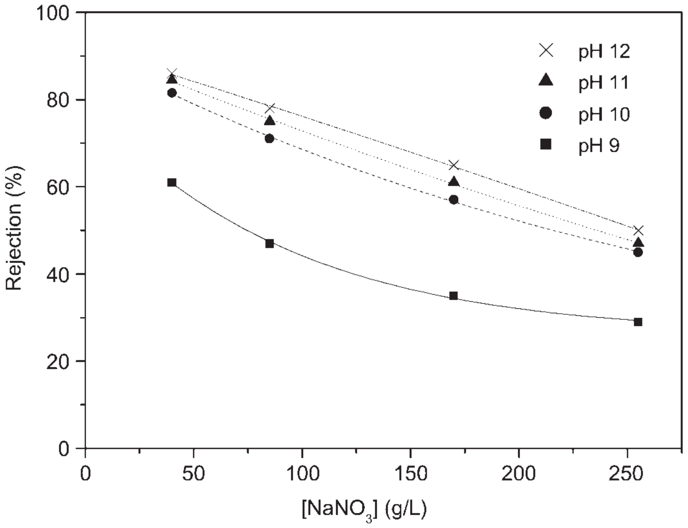

Figure 11. Plot of the rejection of cesium vs. pH and [$NaNO_3$] ([Cs^+] = 0.11 mmol/L; [resorcinarene]/[cesium] = 20; ΔP = 4 bar; T = 20°C).

Though a NF–complexation process, it allowed us to separate traces of cesium in a highly salted aqueous medium with resorcinarene as ligand. Cesium complex rejection of 80% is obtained at pH 12 ($\log K'^{\mathrm{pH12}}_{\mathrm{CsL}} = 6.05$) for $[\mathrm{NaNO_3}] = 0.47\,\mathrm{mol/L}$ and $[\mathrm{resorcinarene}] = 2.11\,\mathrm{mmol/L}$, which is the limit pH condition for this organic-NF membrane. Unfortunately, at this pH, the resorcinarene is readily degraded whatever the $NaNO_3$ concentration. On the other hand, at pH 9, resorcinarene is stable more than 30 days even with strong salinity. Despite the good stability of the resorcinarene at pH 9, an adsorption and a particle deposition of the resorcinarene on the membrane reduced the permeate flux and cesium complex rejection. Between pH 10 and 11, the resorcinarene is stable up to 8 days, and cesium rejection of 80% is obtained in the presence of sodium ($[\mathrm{NaNO_3}] = 0.47\,\mathrm{mol/L}$) by using a $[\mathrm{resorcinarene}]/[\mathrm{Cs^+}]$ ratio of 20 at pH 11 and 25 at pH 10.

This study was set up to separate a few mmole of cesium in the presence of 3 mol/L of $NaNO_3$. In reality, a few μmole of cesium must be separated after cleaning or decontamination[2] of the nuclear installation; therefore, some μmole of resorcinarene will be necessary.

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