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# Evaluation of solid-supported room-temperature ionic liquids containing crown ethers as media for metal ion separation and preconcentration



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## ABSTRACT

Extraction chromatographic (EXC) resins incorporating an appropriate crown ether in an oxygenated organic solvent such as 1-octanol are well established as sorbents for the analytical-scale separation and preconcentration of radiostrontium from a variety of sample types. Recent solvent extraction studies employing crown ethers in various 1-alkyl-3-methylimidazolium-based ( $C_nC_1im^+$ ) room-temperature ionic liquids (RTILs) indicate that under certain conditions, distribution ratios ( $D_{Sr}$ ) for strontium far in excess of those observed with conventional organic solvents are observed. To determine if this increase in liquid–liquid extraction efficiency will lead to improved strontium sorbents, several EXC resins and sol-gel glasses incorporating di-*tert*-butylcyclohexano-18-crown-6 (DtBuCH18C6) in either 1-decyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ( $C_{10}C_1imTf_2N$ ) or the related hydroxyalkyl-functionalized IL 1-(12-hydroxydodecyl)-3-butylimidazolium bis[(trifluoromethyl)sulfonyl]imide ( $C_{12}OH C_4im Tf_2N$ ) were prepared and characterized. Unexpectedly the performance of these materials was not uniformly better than that of a conventional EXC resin, an apparent result of the greater viscosity of the ionic liquids and the lower solubility of the crown ether in ILs versus conventional organic solvents.

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## 1. Introduction

Extraction chromatography, a type of liquid chromatography in which the stationary phase comprises a metal ion extractant or a solution of the extractant in an appropriate diluent sorbed on an inert (often, polymeric) support, has proven to be of extraordinary utility in the development of methodology for the determination of a variety of radionuclides in environmental (e.g., soil) and biological (e.g., bioassay) samples [1–3]. Despite its many advantages, however, extraction chromatography suffers from several significant limitations [2–4]. First, because the extractant is sorbed rather than covalently bonded to the support, the physical stability of extraction chromatographic (EXC) resins can be inadequate for many applications. In addition, the capacity of typical EXC sorbents is rather limited, often to only a few mg/mL of bed volume. As a result, inconveniently large columns may be required if extractant saturation (i.e., column overload) is to be avoided. Finally, the

retention of metal ions on certain EXC materials is often insufficient, even in the absence of competing ions that might be expected to consume a significant fraction of the sorption sites on the material. For example, although an EXC resin selective for radiostrontium [5–7] has long been commercially available (i.e., Sr resin, EiChroM Technologies), its modest strontium retention makes it poorly suited for large-volume samples and complicates efforts to miniaturize chromatographic separations employing it.

Prior work has shown that metal ion extraction by crown ethers such as that on which the commercial strontium resin is based (di-*tert*-butylcyclohexano-18-crown-6, hereafter abbreviated as DtBuCH18C6) is strongly influenced by the organic solvent in which the extractant is dissolved [8,9]. For example, strontium extraction into a solution of dicyclohexano-18-crown-6 (DCH18C6) and by analogy, its retention on a crown ether-based EXC resin [5,10], has been found to increase as the molecular weight of the solvent is decreased within a given diluent family, the apparent result of the greater solubility of water in lower molecular weight solvents and the accompanying increase in the ease of solvating the co-extracted anion [8]. As a compromise between the need to maximize strontium retention and to minimize the loss of the crown ether/diluent mixture comprising the

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stationary phase to solubilization in the mobile phase during a separation, 1-octanol is employed as the stationary phase solvent in the commercial resin [5,6]. Recent work suggests that better results, in particular far stronger retention of strontium, might be achieved by employing ionic liquids (ILs), a novel class of solvents typically comprising a bulky, asymmetric organic cation in combination with any of a wide variety of organic or inorganic anions [11] as the basis of the stationary phase. Specifically, various studies have shown that under certain conditions, metal ion extraction efficiencies far exceeding those seen with conventional, molecular solvents can be obtained in liquid–liquid systems employing solutions of an appropriate extractant in any of a variety of ILs [12–14]. For example, using solutions of DCH18C6 in *N,N'*-dialkylimidazolium-based ILs, Dai et al. [12] have demonstrated that strontium distribution ratios ( $D_{Sr}$ , defined as the ratio of the total concentration of strontium in the organic phase to that in the aqueous phase at equilibrium,  $[Sr]_{org,eq}/[Sr]_{aq,eq}$ )  $10^4$  times larger than those observed in 1-octanol can be obtained. This suggests that an EXC resin employing an appropriate IL as a component of the stationary phase may provide strontium ion retention significantly greater than that obtained with conventional EXC resins.

In the past decade, a number of metal ion sorbents have been described that comprise an ionic liquid dispersed in/on a solid support [15–25]. Much less common are those in which an ionic liquid is employed as the diluent for a supported metal ion extractant [26–30]. In this report, we describe the preparation and preliminary characterization of several strontium sorbents incorporating a mixture of a crown ether and various *N,N'*-dialkylimidazolium-based ILs, supported in either a porous polymer matrix, as is often done in extraction chromatography, or a sol-gel glass. Unexpectedly the results obtained indicate that the performance, in particular the strontium retention, of these new materials is not necessarily superior to that of the conventional commercial EXC resin.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Reagents

Dicyclohexano-18-crown-6 (DCH18C6) was obtained as a mixture of the *cis-syn-cis* (A) and *cis-anti-cis* (B) isomers from Parish Chemical Company (Orem, UT). The 4,4'(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) was obtained from Eichrom Technologies, Inc. (Darien, IL) and unless otherwise noted, used without further purification. For liquid–liquid extraction studies, where interpretation of the results was facilitated by the use of a single isomeric form of the crown ether, a 0.5 M solution in hexane was contacted with twice its volume of 1 M perchloric acid to precipitate out the 4z,5'z *cis-syn-cis* form. Amberchrom™ CG-71m was purchased from Rohm and Haas (Philadelphia, PA) and pretreated as previously described [31]. The tetramethyl orthosilicate (TMOS) and 1-octanol were obtained from Alfa Aesar (Heysham, UK), while the formic acid (98%) was obtained from Sigma-Aldrich (St. Louis, MO). All were used as received. Optima™ grade nitric acid and HPLC grade methanol were obtained from Fisher Scientific Company (Waltham, MA). The Sr-85 and Na-22 radiotracers were purchased from Perkin Elmer Corporation (Shelton, CT) as the respective chlorides and converted to the nitrate form by repeated evaporation to dryness in the presence of nitric acid. All water was obtained from a Milli-Q2 system and had a specific resistance of at least 18 MΩ-cm. The ionic liquids employed in this work, 1-decyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ( $C_{10}C_1imTf_2N$ ) and 1-(12-hydroxydodecyl)-3-butylimidazolium bis

[(trifluoromethyl)sulfonyl]imide ( $C_{12}OHC_4imTf_2N$ ), were prepared by reaction of the corresponding bromides with  $LiTf_2N$  and purified using methods described previously [11,32,33]. Sample purity was verified by  $^1H$ - and  $^{13}C$  NMR (DMSO), as detailed in previous reports [11,32,33]. The NMR spectra were acquired on a Bruker DPX300 NMR spectrometer operating at 300.13 MHz for proton and 75.47 MHz for carbon-13, and equipped with a z-gradient broadband (BBO) probe. Spectra were obtained using solutions in dimethylsulfoxide- $d_6$  (Aldrich, 99.96 atom% D), and all chemical shifts were reported relative to tetramethylsilane.

### 2.2. Methods

#### 2.2.1. Liquid-liquid extraction studies

The distribution of the radiotracer between aqueous and organic phases of interest was determined by equilibrating equal volumes of a tracer-spiked nitric acid solution and either 1-octanol or an ionic liquid. Prior to the distribution measurement, the organic phase was pre-equilibrated *via* two contacts with twice its volume of an appropriate acid solution. From the measured activity of the aqueous and organic phases after equilibration, determined via gamma spectroscopy according to standard procedures on a Perkin-Elmer 2480 Automatic Gamma Counter, the distribution ratio of strontium (or sodium) was calculated from the equation:

$$D_M = [M]_{org,eq}/[M]_{aq,eq}$$

#### 2.2.2. Polymer-supported IL-crown ether mixtures

The EXC resins comprising polymer-supported IL-crown ether mixtures were prepared in a manner analogous to that described previously for mixtures of crown ethers and conventional organic solvents [5,6].

#### 2.2.3. Sol-gel-encapsulated IL-crown ether mixtures

To synthesize the silica-based EXC materials, an acid-catalyzed sol-gel procedure was employed [34]. In a typical preparation, DtBuCH18C6 (50 mg) was dispersed into a mixture of TMOS (1 mL) and formic acid (2 mL). This route yielded a “solvent-less” (*i.e.*, no diluent added) sorbent. To determine the impact of the presence of a solvent, the same route for preparation was followed, but neat DtBuCH18C6 was replaced with a 1 M solution of the crown ether in either the IL or 1-octanol. For all preparations, the quantity of DtBuCH18C6 used was maintained at 50 mg. After a week of standing, during which time gelation and the volatilization of the  $CH_3OH$  and  $HCOOCH_3$  hydrolysis products occurred, a monolithic glass composite consisting of DtBuCH18C6 or its solution in the IL or 1-octanol entrapped in the silica network [35] was obtained. The composite glass material was crushed and sieved to collect material of the desired size range ( $\sim 50$ – $100 \mu m$  diameter) for subsequent metal ion uptake experiments. Following sieving, the ground material was examined by scanning electron microscopy using a Hitachi Model S-4800 field emission SEM.

#### 2.2.4. Sorbent characterization: equilibrium metal ion uptake

Solid–liquid (weight) distribution ratios ( $D_w$ ) for strontium and sodium were determined radiometrically using  $^{85}Sr$  and  $^{22}Na$  radiotracers. Specifically, the sorption of the tracer from nitric acid solutions by the resins was measured by contacting a known volume (typically 1.0 mL) of tracer-spiked acid solution of appropriate concentration with a known mass of resin. The ratio of the aqueous phase volume (mL) to the weight (g) of the chromatographic material ranged from 40–50. (This ratio is determined primarily by the need to produce an easily measured decrease in the aqueous activity by contact with the resin.) Contact times of two and four hours (with occasional swirling) were employed for

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