Chinese Chemical Letters Vol. 15, No. 10, pp 1219-1222, 2004
http://www.imm.ac.cn/journal/ccl.html

Extraction of Cesium from the Irradiated Nuclear Waste by 4(5),4′(5′)-Bis[1-hydroxyalkylbenzo]-21-crown-7

Ying DU, Wen Jun CHEN, Sheng Ying QIN*

Department of Chemistry, Sichuan University, Chengdu 610064

Abstract: 4(5),4′(5′)-Bis[1-hydroxyalkylbenzo]-21-crown-7 (**A**-**C**) have been synthesized by two-step reactions from dibenzo-21-crown-7 (DB21C7). Extraction of cesium cation from nitric acid solutions by **A-C** has been investigated in nitromethane. Under the conditions of various concentration of HNO_3 or $NaNO_3$, the extractabilities of **A** and **B** were superior to that of DB21C7.

Keywords: 4(5),4′(5′)-Bis[1-hydroxyalkyl]dibenzo-21-crown-7, extraction, cesium.

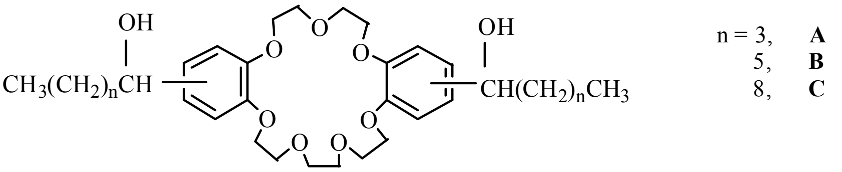
The fission product ^{137}Cs accounts for a large fraction of the radioactivity in high-level nuclear waste (HLW). Because of the hazard to environment and the widespread application of ^{137}Cs gamma radiatior[1], a need has arisen to develop improved methods for the removal and recovery of radiocesium from these wastes. Reports have shown that some calixcrown compounds may be highly selective for Cs cation[2], but, since the synthesis of them is difficult and the cost is high, it might obviate their use practically. So work to study new extractants with simpler structure is still important. Davis[3] and coworkers reported that certain 4-component organic solutions containing isomer mixture of 4(5),4′(5′)-bis[1-hydroxy-2-ethylhexylbenzo]-18-crown-6 could efficiently extract Cs^+ from strong nitric acid solutions, this appears to give the possibility of developing a practicable solvent extraction process for removal/recovery of ^{137}Cs. However, it has shown that 21-membered crown ethers exhibit more favorable extractability toward Cs^+ than the other membered equivalents[4~7]. So in this report, three new compounds, 4(5),4′(5′)-bis[1-hydroxyalkylbenzo]-21-crown-7 (**A**-**C**), were synthesized, and the extraction efficiency of them for cesium cation was also studied. It might provide useful information on the design and synthesis of new extractants for cesium.

4(5),4′(5′)-Bis[1-hydroxyalkylbenzo]-21-crown-7 (**A**-**C**) were prepared by two- stpe reactions: DB21C7 was diacylated with alkanoic acid in polyphosphoric acid, followed by reduction with sodium borohydride in ethanol. The crude products were recrystallized from ethanol to give the pure **A**-**C**, and characterized by IR, Ms, ^{1}H NMR and elements analysis. The structures of **A**-**C** were shown in **Figure 1**.

---

[*] E-mail: qinshengying@mail.china.com

Figure 1 Structures of the title compounds



A: white solid, yield 68%, m.p. 94~96°C. Anal. calcd. for $C_{32}H_{48}O_9$: (%) C 66.67, H 8.33. Found: C 66.59, H 8.40. IR (KBr, cm^{-1}): 3413, 2930, 2860, 1592, 1510, 1264, 1056, 1138. ^1H NMR ($CDCl_3$, δ_H ppm): 6.92~6.80(m, 6H), 4.60~4.54(t, 2H, J=6.0Hz), 4.20~3.86(m, 20H), 2.18(s, 2H), 1.79~1.24(m, 12H), 0.9~0.84(t, 6H, J=6.0Hz). MS *m/z*: 576(M^+).

B: white solid, yield 70%, m.p. 96~98°C. Anal. calcd. for $C_{36}H_{56}O_9$: (%) C 68.35, H 8.86. Found: C 68.41, H 8.82. IR (KBr, cm^{-1}): 3406, 2928, 2843, 1591, 1515, 1270, 1051, 1141. ^1H NMR ($CDCl_3$, δ_H ppm): 6.88~6.78(m, 6H,), 4.57~4.50(t, 2H, J=6.2Hz), 4.17~3.81(m, 20H), 2.31(s, 2H), 1.82~1.27(m, 20H), 0.92~0.87(t, 6H, J=6.1Hz). MS *m/z*: 633(M^+).

C: white solid, yield 76%, m.p. 95~97°C. Anal. calcd. for $C_{42}H_{68}O_9$: (%) C 70.39; H 9.50. Found: C 70.45, H 9.42. IR (KBr, cm^{-1}): 3411, 2921, 2857, 1592, 1514, 1260, 1061, 1140. ^1H NMR ($CDCl_3$, δ_H ppm): 6.91~6.63(m, 6H), 4.59~4.48(t, 2H, J=6.5Hz), 4.12~3.68(m, 20H), 2.25(s, 2H), 1.85~1.16(m, 32H), 0.91~0.85(t, 6H, J=6.3Hz). MS *m/z*: 716(M^+).

Distribution behavior of Cs was investigated by using ^{134}Cs as radiotracer. Distribution ratios (D_{Cs}) were determined by measuring the γ-activity of both organic and aqueous phases. The solvent-extraction procedures were as reported[8].

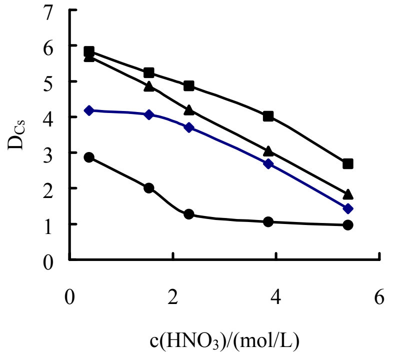
The effect of nitric acid concentration in aqueous phase on the extraction of Cs was shown in **Figure 2**. Reduce of the extraction for cesium was found along with the increase of the nitric acid concentration, because the competition-extraction effect and the salt-out effect caused by nitric acid both existed. Varying the chain length of the substituents on the benzo groups of DB21C7 showed significant effect on the D_{Cs}, the shorter side chain was superior to the longer one. The D_{Cs} of **C** was even inferior to DB21C7, this was in accordance with Davis′ results[3].

Waste solution produced by post-processing of irradiated nuclear fuel contains high concentration of $NaNO_3$. The latter could be extracted in a small extent by crown extractant, and it is a main trouble for the extraction of cesium. So cesium selectivity over sodium is especially important. The effect of sodium nitrate concentration in aqueous phase on the extraction of Cs was shown in **Figure 3**.

The D_{Cs} decreased greatly with the increase of sodium nitrate concentration. It reflects the effect of competition extraction of Na^+ to Cs^+. But the D_{Cs} for **A**, **B** were higher than that of DB21C7.

The effect of extractant concentration was clearly shown as **Figure 4**. Plot of $\log D_{Cs}$ *vs*. $\log c(A)_{(equi.)}$ was a straight line with the slope of 1.03. This result indicated that the radio of Cs : crown complex is 1: 1 as expected.

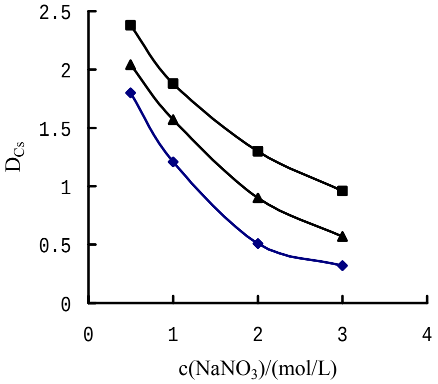
Figure 2 Effect of nitric acid concentration in aqueous phase on D_{Cs}



organic phase: 1.00×10^{-2} mol/L crown in CH_3NO_2 aqueous phase: 4.75×10^{-5} mol/L $CsNO_3$, various conc. of HNO_3

◆-DB21C7；■-A； ▲-B；●-C

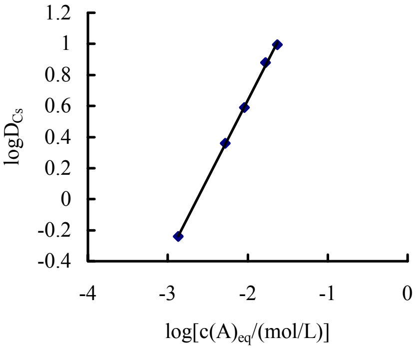
Figure 3 Effect of sodium nitrate concentration on D_{Cs}



organic phase: 1.00×10^{-2} mol/L crown **A** in nitromethane aqueous phase: 2.00 mol/L HNO_3, various conc. of $NaNO_3$, 4.75×10^{-5} mol/L $CsNO_3$

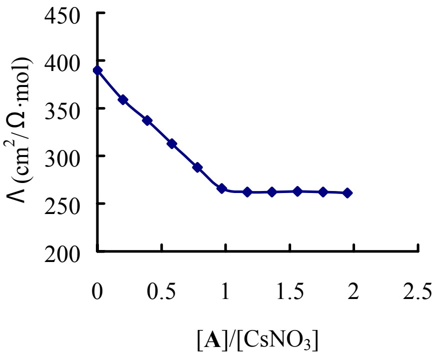
◆-DB21C7；■-A； ▲-B

Figure 4 Effect of extractant in organic phase



organic phase: various conc. of **A** in nitromethane aqueous phase: 2.00 mol/L HNO_3, 4.75×10^{-5} mol/L $CsNO_3$

Figure 5 Plot of equivalent Λ vs. the ratio [A]/[CsNO3] in nitromethane



[**A**] : 1.00×10^{-4} mol/L [$CsNO_3$]: 5.13×10^{-5} mol/L

The composition of the complexes were determined indirectly by measuring the conductance of cesium nitrate-crown**A** in nitromethane at 20±1℃. Plot of equivalent conductance Λ *vs*. the ratio [**A**]/[$CsNO_3$] was shown in **Figure 5**. It was considered from the break-point of the plot that **A** formed a 1:1 complex with cesium, and the extraction was belong to ion-pair extraction.

Acknowledgment

This work is supported by the National Natural Science Foundation of China (Project No. 2007205).

References

1. R. M. Cornell, *J. Radioanal. Nucl. Sci. Tech.*, **1993**, *171*, 483.
2. R. A. Sachleben, P. V. Bonnesen, T. Descazeaud, *et al.*, *Solvent Extr. Ion. Exch.*, **1999**, *17*(6), 1445.
3. I. H. Gerow, J. E. Smith, M. W. Davis, *Sep. Sci. Technol.,* **1981**, *16*(5)., 519.
4. B. A. Moyer, Y. P. Deng, Y. F. Sun, *et al.*, *Solvent Extr. Ion Exch.*, **1997**, *15*, 791.
5. R. A. Sachleben, Y. P. Deng, D. R. Bailey, *et al.*, *Solvent Extr. Ion Exch.*, **1996**, *14*, 995.
6. V. Lamare, D. Haubertin, J. Golebiowski, *et al.*, *J. Chem. Soc. Perkin Trans.,* **2001**, *2*(1), 121.
7. V. M. Abashkin, E. A. Filippov, A. K. Nardova, *et al.*, *Res. Soc. Symp. Proc.,* **1999**, 566.
8. L. Zhu, Z. Q. Liu, W. J. Chen, *et al.*, *J. Radioanal. Nucl. Chem. Articles*, **1996**, *205*(1), 49.

Received 17 September, 2003