THE USE OF POLYETHERS IN THE TREATMENT
OF ACIDIC HIGH ACTIVITY NUCLEAR WASTES
First Progress Report

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ABSTRACT

The objective of this work is to develop a solvent extraction system for treating acidic high activity nuclear wastes in order to remove 99.9% of the cesium and strontium. The removal of 99.9% will lower the relative toxicity⁽¹⁾ of 10 year old waste by a factor of 10^3 . In order to accomplish this, we are screening a series of macrocyclic polyethers "crown compounds" which have the ability to form organic soluble complexes with the alkali metals (Cs^{+1}) and the alkaline earth metals (Sr^{+2}). Thus far five "crown" compounds have been tested for solubility in both carbon tetrachloride and kerosene each solvent containing a range of tributyl phosphate (TBP) concentrations. Also distribution coefficients of both cesium and strontium have been measured between these organic phases with the individual crown compounds dissolved in them and an aqueous phase containing nitric acid concentrations varying from .0125M to 2M.

The results of tests thus far have been negative in that we have not achieved sufficient extraction of either Cs^{+1} or Sr^{+2} into the organic phase to make a solvent extraction process feasible. The highest distribution coefficient obtained (organic/aqueous)⁽²⁾ was $.04 \pm .02$ for both Sr^{+2} and Cs^{+1} whereas we would like a distribution coefficient of unity. The problem seems to lie in the low solubility of the "crowns" in the organic phases tested and the apparent ability of the "crowns" to distribute into the aqueous phase and complex the metal as indicated by a rise in the total organic content of the aqueous in distribution experiments when either Cs^{+1} or Sr^{+2} is present in the aqueous phase.

A study of the solubility data shown in Tables I and II indicates that the addition of aliphatic character to the "crowns" improves their organic solubility whereas aromatic addition (V, Figure 2) decreases their organic solubility. With

(1) Relative toxicity is the ratio of the concentration in the waste to maximum permissible concentration in public zone waste. See DP-MS-73-58 by R. F. Bradley, W. H. Hale and R. M. Wallace of the Savannah River Laboratory, E. I. du Pont de Nemours, Aiken, South Carolina 29801.

(2) Obtained by equilibrating equal volumes of aqueous and organic.

this in mind, a new "crown", 4, 4'-di-decanoylbenzo 24-crown-8, was ordered from the Parish Chemical Company in Provo, Utah. The structure of this material is shown in Figure 1. It had never been synthesized before.

Parish Chemical has reported that they have made this compound in good yield and that it is very soluble in hot hexane, and is also soluble in ethyl acetate, benzene and warm carbon tetrachloride. We have just received five grams for testing and will receive another forty five grams shortly.

This approach appears promising, and other compounds of this type will be tested in the future since it is unlikely that this is the one best suited to meet all of the requirements of nuclear processing.

PERSONNEL

1. The principal investigator (Milton W. Davis, Jr.) devoted six full time summer months and 20% of each of the fifteen academic months that the project has been underway.
2. Irene Gerow - First year graduate student working for a Ph.D. has spent six full time summer months and twenty hours per week during the fifteen academic months that the project has been underway.
3. Robert Figel - First year graduate student spent 20 hours per week for eight academic months before leaving project.

RESEARCH RESULTS

Five "crown" compounds have been tested for possible use in a solvent extraction process to extract cesium (Cs^{+1}) and strontium (Sr^{+2}) into an organic phase from an aqueous phase containing nitric acid. These "crowns" are listed below.

	<u>Crown</u> ⁽³⁾	<u>Melting Point</u>
I	dibenzo 24-crown-8 ⁽⁴⁾	103-104°C
II	dicyclohexyl 18-crown-6 (96% pure)	liquid at 25°C
III	4,4'-di-tert-butylbenzyl 24-crown-8	waxy
IV	4,4'-di tert-butylcyclohexyl 24-crown-8	liquid at 25°C
V	di(2',3' naphthyl) 24-crown-8 ⁽²⁾	191°C

The choice of 24-crown-8 compounds resulted from previous work by Frensdorff⁽⁵⁾ indicating that this size "crown" would be one of the best for Cs^{+1} complexation. The dicyclohexyl 18-crown-6 was very soluble in the aqueous phase and was eliminated for this reason. Some 21-crown-7 compounds have been considered but they are more difficult to synthesize and more costly to buy so for the time being we are not testing them.

As the organic phase, the "crowns" are being dissolved in either CCl_4 or kerosene with varying concentrations of tributyl phosphate (TBP). The aqueous phase consists of a range of HNO_3 concentrations (.0125M-2M) containing either Sr^{+2} or Cs^{+1} at a concentration ranging from .0005M to .01M with most tests being carried out at .001M. A few of the recent tests contained $\text{Al}(\text{NO}_3)_3$ in the aqueous phase as a salting agent from .13M-1M. A few tests also included thenoyltrifluoroacetone (HTTA) in the organic phase in an attempt to supply an organic soluble anion to satisfy the valance requirements of the extracted metal. The HTTA was added to the organic phase at a concentration of either .05M or .10M.

(3) See Figure 2 for the structure of each "crown" compound.

(4) These compounds were synthesized at the University of South Carolina because of the relative ease of synthesis and much lower cost involved.

(5) H. K. Frensdorff, JACS, 93, 600 (1971).

Samples of about five grams of the dibenzo 24-crown-8 and the di(2',3' naphthyl) 24-crown-8 were also sent to Mr. R. R. Shoun of the Chemical Development Section of ORNL for testing.

The structures of the five "crown" compounds already tested are shown below.

TABLE I

Solubility of "Crown" Compounds in Organic Solvents
at 25°C

<u>Solvents</u>	<u>Solubility, (7) moles/liter</u>	<u>Compound (6)</u>
.1M TBP in kerosene	6.4×10^{-4}	I
100% TBP	13×10^{-4}	
CCl ₄	200×10^{-4}	
.1M TBP in kerosene	500×10^{-4}	II (96% pure)
.1M TBP in kerosene	37×10^{-4}	III
1.83M TBP in kerosene	229×10^{-4}	
100% TBP	310×10^{-4}	
CCl ₄	500×10^{-4}	
.13M TBP in kerosene	700×10^{-4}	IV
CCl ₄	$.90 \times 10^{-4}$	V

TABLE II

Solubility of "Crown" Compounds in .1M HNO₃
at 25°C

<u>Solubility, (7) moles/liter</u>	<u>Compound (6)</u>
3.5×10^{-4}	I
220×10^{-4}	II
$.86 \times 10^{-4}$	III
9.7×10^{-4}	IV
$.90 \times 10^{-4}$	V

(6) See Figure 2 for structure of each "crown" compound.

(7) Estimated percentage error of solubility data is $\pm 5\%$.

The measured distribution coefficients for both Sr^{+2} and Cs^{+1} never exceeded $.04 \pm .02$ (organic/aqueous) over the whole range of solutions studied. It is clear now that long aliphatic chains attached to the "crown" increase organic solubility and the future thrust of the research effort should involve the procurement and study of this type of compound.

PUBLICATIONS

No publications have resulted from this work as yet.

FIGURE 1

I

II

III

IV

V

FIGURE 2