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

The Use of 24-Crown-8's in the Solvent Extraction of $CsNO_3$ and $Sr(NO_3)_2$

Irene H. Gerow[a]; M. W. Davis Jr.[a]
[a] COLLEGE OF ENGINEERING, UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA

To cite this Article Gerow, Irene H. and Davis Jr., M. W.(1979) 'The Use of 24-Crown-8's in the Solvent Extraction of $CsNO_3$ and $Sr(NO_3)_2$', Separation Science and Technology, 14: 5, 395 — 414
To link to this Article: DOI: 10.1080/01496397908058093
URL: http://dx.doi.org/10.1080/01496397908058093

SEPARATION SCIENCE AND TECHNOLOGY, 14(5), pp. 395–414, 1979

The Use of 24-Crown-8's in the Solvent Extraction of $CsNO_3$ and $Sr(NO_3)_2$

IRENE H. GEROW and M. W. DAVIS, JR.*

COLLEGE OF ENGINEERING
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, SOUTH CAROLINA 29208

Abstract

The feasibility of a solvent extraction process for removing strontium and cesium from acidic high activity nuclear waste is shown. Both strontium and cesium can be extracted from an aqueous HNO_3 phase containing the metal nitrates into an organic phase containing kerosene or CCl_4 as a diluent and complexing agents dissolved in the diluent. The most promising results obtained thus far have required the use of a mixture of three metal complexing agents: tributyl phosphate, di-2-ethylhexyl phosphoric acid, and 4,4′(5′)-di-tert-butylbenzo-24-crown-8. The highest distribution coefficients obtained (organic/aqueous) were 1.45 ± 0.05 for Cs^+ and 200 for Sr^{2+}. The extraction is reversible and is strongly dependent on the pH of the aqueous phase. The metal can be removed from the organic phase by lowering the pH to 1, while raising the pH above 3 causes the metal to return to the organic phase. The utility of this extraction technique for nuclear processing will depend on the radiation stability of the complexing agents and the degree of selectivity obtained when extracting strontium and cesium from mixed fission products.

INTRODUCTION

In 1967 Pedersen (*1*) of DuPont reported the synthesis of a group of metal complexing agents called macrocyclic polyethers or "crown" compounds. These compounds have the rather remarkable property of forming strong complexes with the alkali metals (*2*) (Li^+, Na^+, K^+, Cs^+)

*To whom correspondence should be sent.

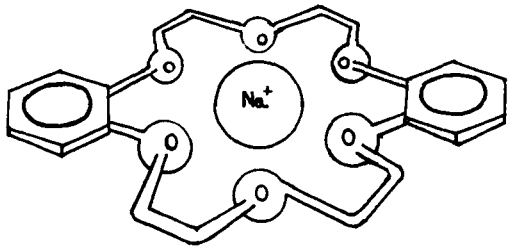

FIGURE 1

and the alkaline earth metals (Ca^{2+}, Sr^{2+}, etc.) (*3*). The structure of the first of these compounds to be made by Pedersen is shown in Fig. 1.

The compound shown is called dibenzo-18-crown-6 according to Pedersen's terminology, where 18 refers to the number of carbon plus oxygen atoms in the ring or "crown" and 6 refers to the number of oxygen atoms in the "crown." These compounds, which contain more than one benzo group, are nearly insoluble in water but dissolve readily in some organic solvents such as methylene chloride and chloroform. The saturated polyethers such as dicyclohexyl-18-crown-6 are much more soluble in organic solvents than their aromatic precursors.

Solvent extraction studies by Pedersen and Frensdorff (*2*, *4*, *5*) indicated that the amount of alkali metal extracted into the organic phase containing a "crown" compound from an aqueous phase in contact with it is dependent upon the following variables:

(1) The nature of the organic solvent in which the "crown" complexing agent is dissolved.
(2) The anion associated with extracted metal.
(3) The diameter of the "crown" or hole as compared to the diameter of the ion being extracted. For maximum complexing effectiveness the crown diameter should be at least as large as the ionic diameter but not too much larger.
(4) The chemical composition of the aqueous and organic phases.
(5) The nature of the side rings fused onto the main polyether ring.
(6) The pH of the aqueous solution if the "crown" compound is one of those which protonated readily (*6*).

The development of these unusual complexing agents (*7*) may be of great benefit to the nuclear industry if they can be used to remove 99.9% of the Cs^+ and Sr^{2+} from high activity wastes by a solvent extraction

process prior to neutralization. Because of the large amount of Na^+ present in the neutralized waste, which is also complexed by the "crown" compounds, it does not appear feasible to selectively extract ^{137}Cs and ^{90}Sr from neutralized waste. These two radionuclides, with half lives of 30 and 28.8 years, respectively, are the major biological hazards and heat producers in waste which has aged for a few years (see Table 1) (*8*). If these two isotopes could be removed from the fresh acid waste so that only 0.1% or less remained, the hazards of handling and storage of the remaining waste would be reduced by a factor of $\sim 10^3$ while the strontium and cesium could be formed into small volume solids for retrievable storage. If the cesium and strontium could be separated, they could be used commercially as either heat or radiation sources which would allow partial recovery of the processing costs.

TABLE 1[a]

Amounts of Activity in 10-Year-Old Waste and Relative Toxicity Due to Radionuclides

Isotope	Half-life (years)	Total activity[b] (curies)	Relative toxicity[c]
^{90}Sr	28.8	2.0×10^8	2×10^9
^{137}Cs	30.0	2.0×10^8	3×10^7
^{147}Pm	2.6	6.7×10^7	1×10^6
^{106}Ru	1.0	3.5×10^5	1×10^5
^{238}Pu	89	1.7×10^5	1×10^5
^{244}Cm	18.1	1.2×10^3	6×10^4
^{151}Sm	90	4.6×10^6	4×10^4
^{239}Pu	2.4×10^4	1.7×10^4	1×10^4
^{129}I	1.6×10^7	31	1.7×10^3
^{99}Tc	2.1×10^5	3.0×10^4	300
^{79}Se	7×10^4	280	120
^{135}Cs	2.0×10^8	3.1×10^3	100
^{126}Sn	10^5	1×10^3	100
^{93}Zr	9.5×10^5	6.7×10^3	30
^{94}Nb	2×10^4	3.2	13
^{107}Pd	7×10^8	26	3
^{158}Tb	150	0.5	4×10^{-5}

[a] This table was taken from 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.

[b] Assumed as a basis for this report and do not represent the actual quantities (classified) to be processed.

[c] Ratio of concentration in waste to maximum permissible concentration in public zone water.

This paper reports work done to develop a solvent extraction process in which the organic diluent was restricted to either CCl_4 or kerosene with tributyl phosphate (TBP) as one complexing agent. Kerosene was chosen in order to develop a process compatible with the Purex process which is used for plutonium and uranium purification at the Savannah River Plant. A variety of 24-crown-8 compounds was tested to determine the effect of side-chain length and structure on organic solubility and complexation ability. The effects of anion size, shape, and structure, and aqueous phase pH and composition on the extraction process were also studied. The 24-crown-8's were chosen because data by earlier investigators had indicated good Cs^+ complexing ability for this size crown. The structures of all the crowns tested are shown in Fig. 2.

EXPERIMENTAL

Aqueous phases tested were composed of various HNO_3 concentrations ranging from pH 5.5 to 3 *M* and containing 0.001 *M* $CsNO_3$ or $Sr(NO_3)_2$. Tests using 0.001 *M* KNO_2 added to the aqueous phase in addition to the $Cs(NO_3)$ or $Sr(NO_3)_2$ were also made.

Organic phases tested were composed of the crowns dissolved in either CCl_4 or kerosene with varying concentrations of TBP. In some tests as much as 50% of di-2-ethylhexyl phosphoric acid (DEHPA) was also added to the organic phase.

For the determination of batch distribution data of the metals, equal volumes of the two phases were shaken together for 1 hr at 330 oscillations/min on a wrist-action shaker manufactured by Burrell Corp., Pittsburgh, Pennsylvania. Shaking was followed by centrifugation after which the aqueous phases were isolated for analysis. The temperature was held at $25 \pm 2°C$.

The metal concentration in the aqueous phase was determined using a Jarrell-Ash Model 530 Atomic Absorption Spectrophotometer. Aqueous samples were shaken with organic phases either with or without crown, and the metal concentrations determined after centrifugation to separate the phases. The difference in aqueous phase metal concentrations between the samples with crown and the ones without crown was interpreted as the amount of metal complexed by the crown. Selected organic samples were then shaken with an equal volume of a fresh aqueous phase to extract the metal back into the aqueous phase in order to check the total material balance on the metal. Results agreed within $\pm 10\%$.

The pH of the aqueous phases was determined by using a Corning pH

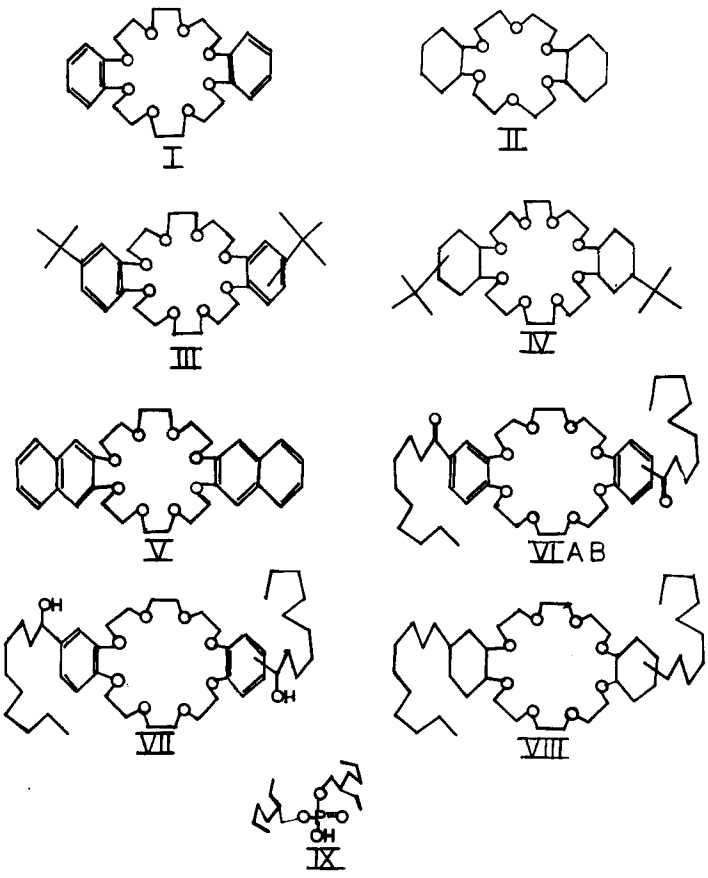

FIG. 2. Crown and phosphoric acid structures.

Meter Model 10. Acid concentrations greater than 0.1 *M* were titrated with dilute NaOH solution using phenolphthalein as an indicator.

Solubilities of crowns in organic phases were determined by adding small increments of the organic phase to a known amount of crown, shaking up to 30 min between additions of organic until the crown dissolved. Most were checked twice.

Solubility of the crowns in various aqueous phases was determined by equilibrating the crown alone with the aqueous phase. Knowing the crown structure and with data obtained as ppm CO_2 from the Beckman

Model 915A Total Carbon Analyzer for known sample volumes, the crown solubility was calculated. The solubility data were reproducible within $\pm 5\%$. Distribution data of the crowns between organic and aqueous phases were determined by equilibrating the organic phase without the crown and the organic phase, of the same composition, with the crown with identical aqueous phases. The aqueous phases were then analyzed using the Beckman Model 915A Total Carbon Analyzer. The difference in the ppm CO_2 in the gases from the oxidized samples was interpreted as being due to the crown concentration. Since this technique often requires subtracting two large numbers, the data are less accurate than the direct solubility determinations. In general, less crown was found in the aqueous phase in the distribution experiments than in the solubility experiments, as might be expected.

The dicyclohexo-18-crown-6 (II) was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. The dibenzo-24-crown-8 (I) and the di-(2′,3′-naphtho)-24-crown-8 (V) were synthesized at the University of South Carolina, Columbia, South Carolina. The rest of the crowns were synthesized by Parish Chemical Co., Provo, Utah. The DEHPA (IX) was obtained from Pfaltz & Bauer, Stamford, Connecticut. A list of the crowns tested together with their melting ranges where appropriate is shown in Table 2.

TABLE 2

Names, Numbers, and Melting Ranges for Structures in Fig. 2

	Name and number	Melting ranges (°C)
I	Dibenzo-24-crown-8	103–104
II	Dicyclohexo-18-crown-6 (96% pure)	Liquid at 25°C
III	4,4′(5′)-Di-tert-butylbenzo-24-crown-8 (BB)	Waxy
IV	4,4′(5′)-Di-tert-butylcyclohexo 24-crown-8	Liquid at 25°C
V	Di(2′,3′-naphtho)-24-crown-8	191
VIA	Bis-(4,4′(5′)-decanoylbenzo)-24-crown-8 (BDB) (less soluble isomer)	85–95
VIB	Bis-(4,4′(5′)-decanoylbenzo)-24-crown-8 (more soluble isomer)	61–70
VII	Bis-(4,4′(5′)-[1-hydroxydecyl]-benzo)-24-crown-8	90–94
VIII	4,4′(5′)-Didecylcyclohexo 24-crown-8	In preparation
IX	Di-2-ethylhexyl phosphoric acid (DEHPA)	Liquid at 25°C

RESEARCH RESULTS

(1) Taking the dibenzo-24-crown-8 as a model for comparison, the addition of a single paraffin side chain such as tertiary butyl to each benzene ring increases organic phase solubility. In this case the solubility in CCl_4 is much greater than in kerosene or TBP (Fig. 3). If the side-chain length is raised to 10 carbon atoms in a straight chain with each chain containing a double-bonded oxygen close to the benzene ring to which it is attached, the organic solubilities are significantly reduced with the kerosene phase now exhibiting the greater solubility (Fig. 3).

If the benzene rings are hydrogenerated to cyclohexyl rings, the solubilities in all organic phases are appreciably increased. This increase in the solubility is plotted in Fig. 4.

Although data are not now available, a side chain containing about seven carbon atoms might be optimum for solvent extraction work if attached to hydrogenated benzene rings. The highest organic solubility together with low aqueous solubility is the goal to give high metal carrying capability with low crown losses to the aqueous phase.

(2) Again taking the dibenzo-24-crown-8 as a model for comparison, an increase in the crown aqueous phase solubility is obtained by increasing the acid strength (Table 3). This effect may be caused by increased protonation of the crown by the stronger acid, thus making it more soluble in the aqueous phase. In support of this argument, all organic phases tested turned a bright yellow color when contacted with 1 *M* or higher concentrations of HNO_3 if any of the crowns tested were present. No color change was observed in the organic phase if a crown was not present.

(3) Solubility studies (Table 4) of the 24-crown-8's in aqueous phases of either 1.5 *M* $CsNO_3$ or 2 *M* $Sr(NO_3)_2$ showed appreciably higher solubility in the 1.5 *M* $CsNO_3$. This would be expected from the much better physical fit of the Cs^+ ion in the 24-crown-8, thus increasing the strength of complexation. The ionic diameters of Cs^+ and Sr^{2+} are 3.38 and 2.26 Å, respectively, while the 24-crown-8 cavity is >4 Å.

(4) Distribution data obtained with 24-crown-8's I, II, III, IV, V, and VIA dissolved in organic phases ranging from pure CCl_4 to pure kerosene with intermediate solutions containing varying

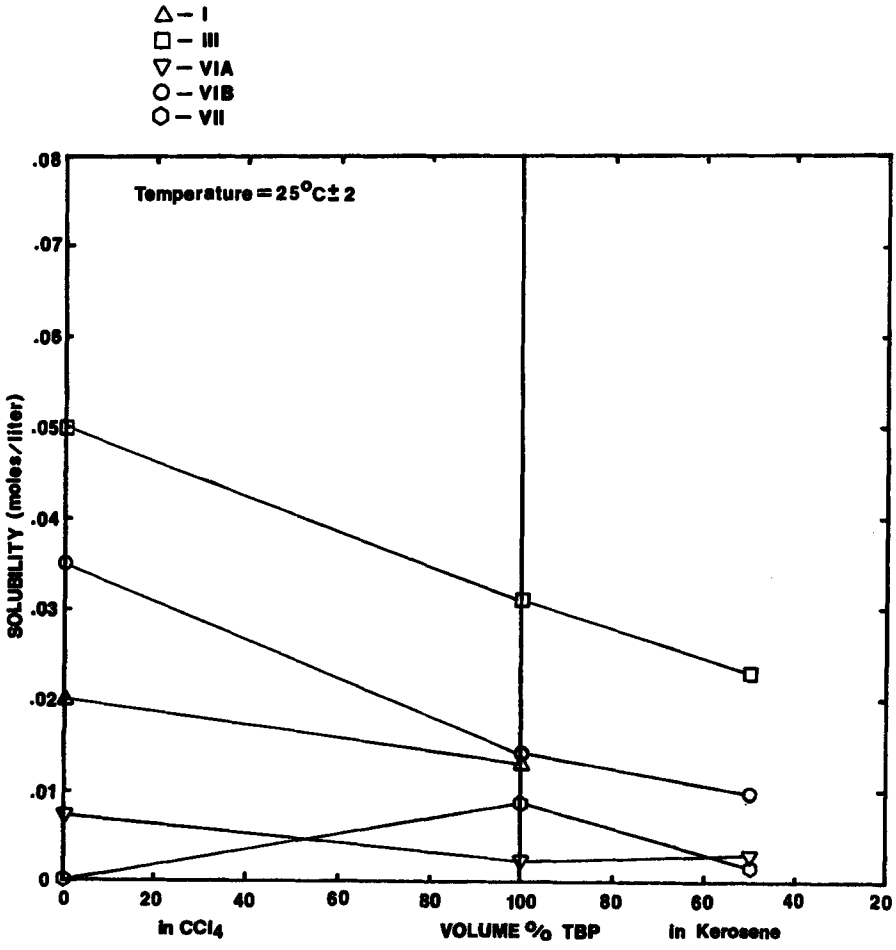

FIG. 3. Solubilities of Crowns I, III, VIA, VIB, and VII as a function of vol-% TBP in both CCl_4 and kerosene.

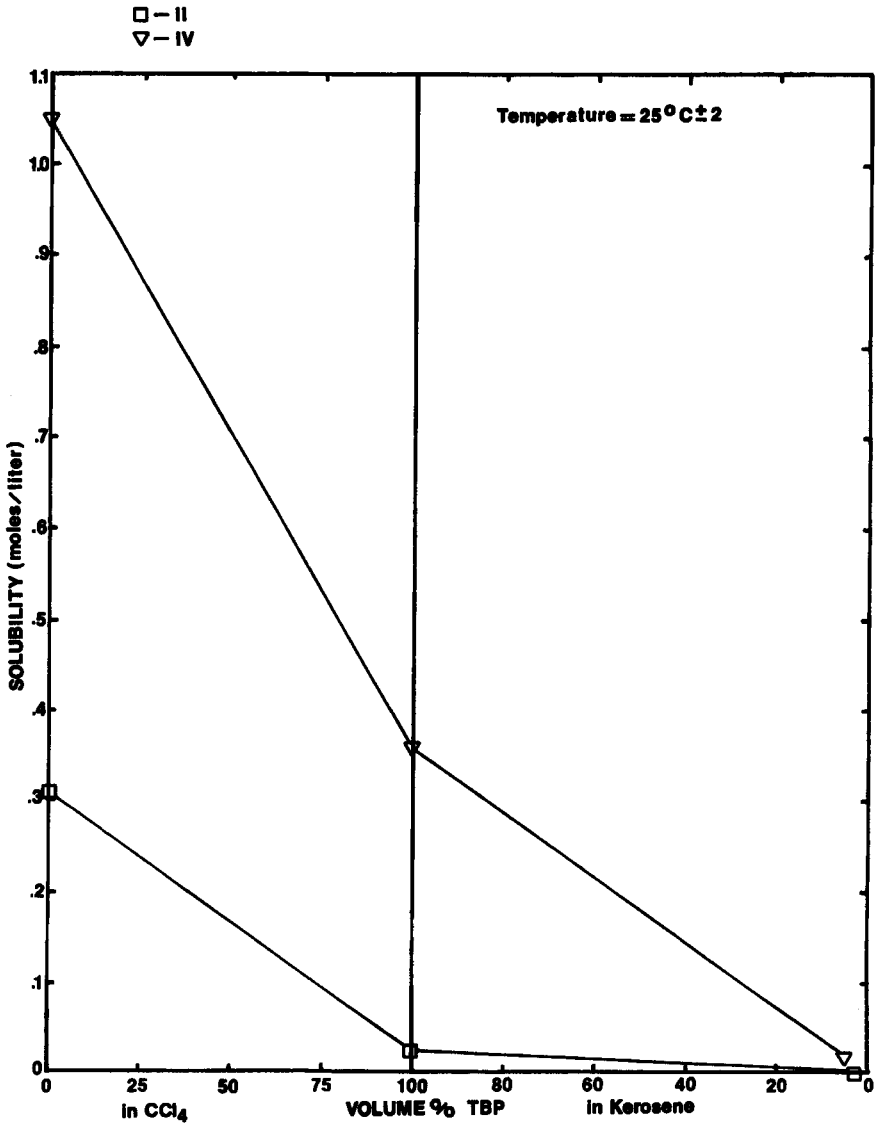

FIG. 4. Solubilities of Crowns I and IV as a function of vol-% TBP in both CCl_4 and kerosene.

TABLE 3

Solubility of "Crown" Compounds in HNO_3 at 25°C

Compound	Solubility (moles/liter)	
	0.10 *M* HNO_3	2 *M* HNO_3
I	3.5×10^{-4}	17.20×10^{-4}
II (96% pure)	220×10^{-4}	—
III	0.86×10^{-4}	54.00×10^{-4}
IV	9.7×10^{-4}	64.00×10^{-4}
V	0.90×10^{-4}	7.90×10^{-4}
VIA	0.36×10^{-4}	4.40×10^{-4}
VIB	1.7×10^{-4}	4.80×10^{-4}
VII	1.9×10^{-4}	1.80×10^{-4}
IX	14.6×10^{-4}	—

TABLE 4

Solubility of "Crown" Compounds in $CsNO_3$ and $Sr(NO_3)_2$ Aqueous Solutions at 25°C[a]

Compound	Solubility (moles/liter)	
	1.5 *M* $CsNO_3$ (saturated)	2 *M* $Sr(NO_3)_2$
I	15.60×10^{-4}	3.03×10^{-4}
III	17.30×10^{-4}	8.25×10^{-5}
IV	52.70×10^{-4}	40.10×10^{-4}
V	1.29×10^{-4}	1.33×10^{-4}
VIA	0.77×10^{-4}	0.53×10^{-4}
VIB	2.71×10^{-4}	0.44×10^{-4}
VII	1.73×10^{-4}	0.87×10^{-4}

[a] Estimated percentage error of solubility data is ±5%.

amounts of TBP when shaken with solutions of HNO_3 containing $CsNO_3$ or $Sr(NO_3)_2$ gave no promise of success. Distribution coefficients (org/aq) ranged from 0 to a maximum of 0.08, which are clearly not adequate for a successful solvent extraction process. The addition of $Al(NO_3)_3$ as a salting agent to the aqueous phase gave no improvement. The use of thenoyltrifluoro acetone (HTTA) in the organic phase to supply an organic soluble anion gave no improvement. The use of a smaller anion, NO_2^-, which in a molecular model study seemed to fit into the crown without as much crowding, did give slight improvement in the distribution coefficients measured but not sufficient for an extraction process.

Investigation of Cl^- as an anion gave distribution coefficients comparable to the NO_3^- system. Again, not satisfactory.

(5) In Figs. 5 and 6 the distribution coefficients (org/aq) of Cs^+ and Sr^{2+}, respectively, are shown as a function of ionic strength. There does seem to be a maximum between ionic strengths of 1 and 2. This is only true when HNO_3 is used to vary the ionic strength since when the HNO_3 is replaced with $Al(NO_3)_3$ the distribution coefficients (org/aq) are very nearly zero. It would appear that this trend is caused by the HNO_3. When 0.001 *M* KNO_2 is added to the aqueous phase, this trend seems more pronounced for Cs^+ (Fig. 5) due to its better fit in the crown. This would seem to suggest that the KNO_2 in the HNO_3 causes the rise in the distribution coefficient while at higher HNO_3 concentrations protonation of the crown reverses the trend, thus leading to the observed maximum.

(6) The use of DEHPA as an organic soluble anion supplier in concentrations as high as 50 vol-% gave Cs^+ distribution coefficients (org/aq) of as high as 0.8 while Sr^{2+} distribution coefficients were as high as 200. These results are shown in Figs. 7–10. There is no crown compound present in the data shown in Figs. 8 and 10, thus showing the effect of DEHPA alone.

(7) A study of the effect of aqueous phase pH on the distribution coefficients of Cs^+ and Sr^{2+} using DEHPA to supply organic soluble anions is shown in Figs. 11 and 12. This study showed that the extraction is reversible and that lowering the pH to 1 causes the metal to enter the aqueous phase. Raising the pH to 3 causes the metal to be extracted into the organic phase. At a pH of 5.5 the Cs^+ distribution coefficient rises to 1.45.

CONCLUSIONS

In view of the demonstrated feasibility of a solvent extraction process for removing both Sr^{2+} and Cs^+ from an aqueous HNO_3 solution to an organic phase reversibly, the course of the work will turn to extraction from mixed synthetic fission products in order to determine the selectivity of the present organic phase complexing agents.

Due to the relatively high aqueous phase pH required to extract Cs^+, other more strongly acidic materials capable of supplying organic anions should be investigated since in a plant process buffering agents might be required to maintain a stable pH in the range of 3 to 4.

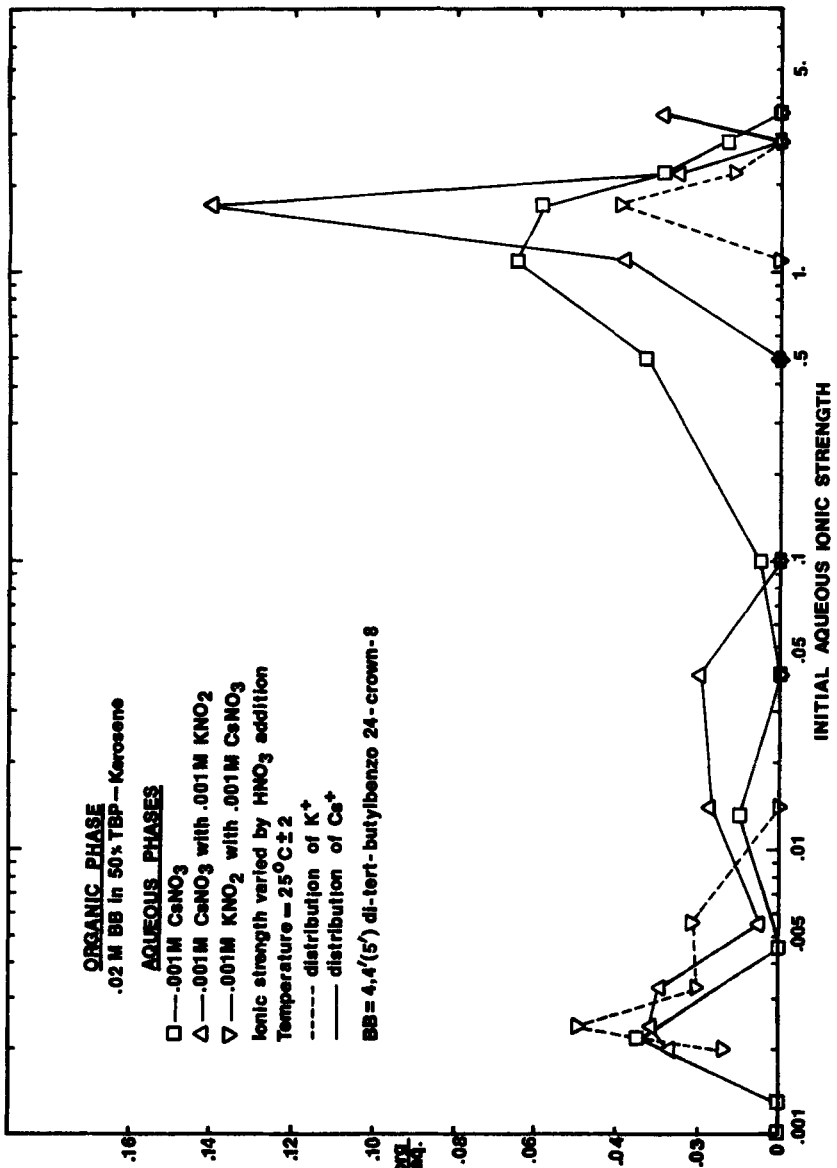

FIG. 5. Distribution of Cs^+ and K^+ as a function of ionic strength.

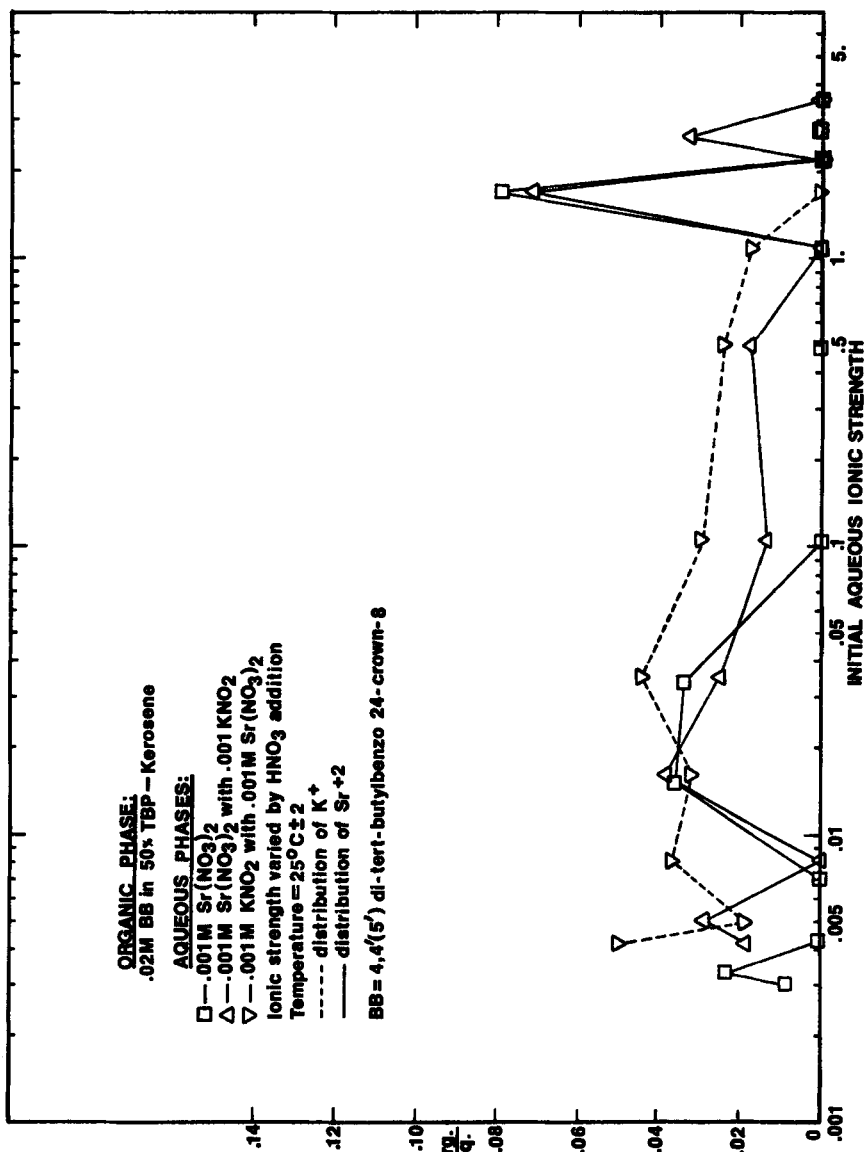

FIG. 6. Distribution of Sr^{2+} and K^+ as a function of ionic strength.

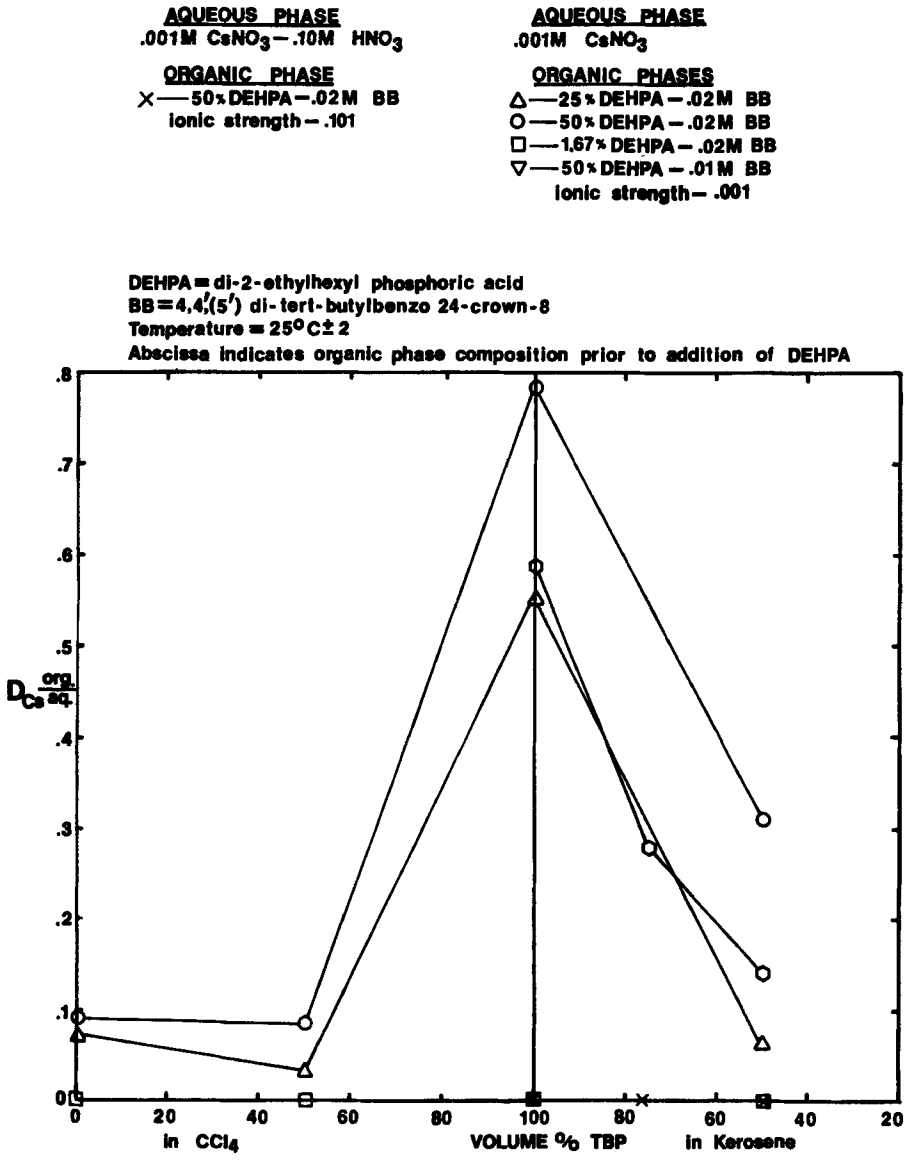

FIG. 7. Distribution of Cs^+ with crown as a function of vol-% TBP and DEHPA.

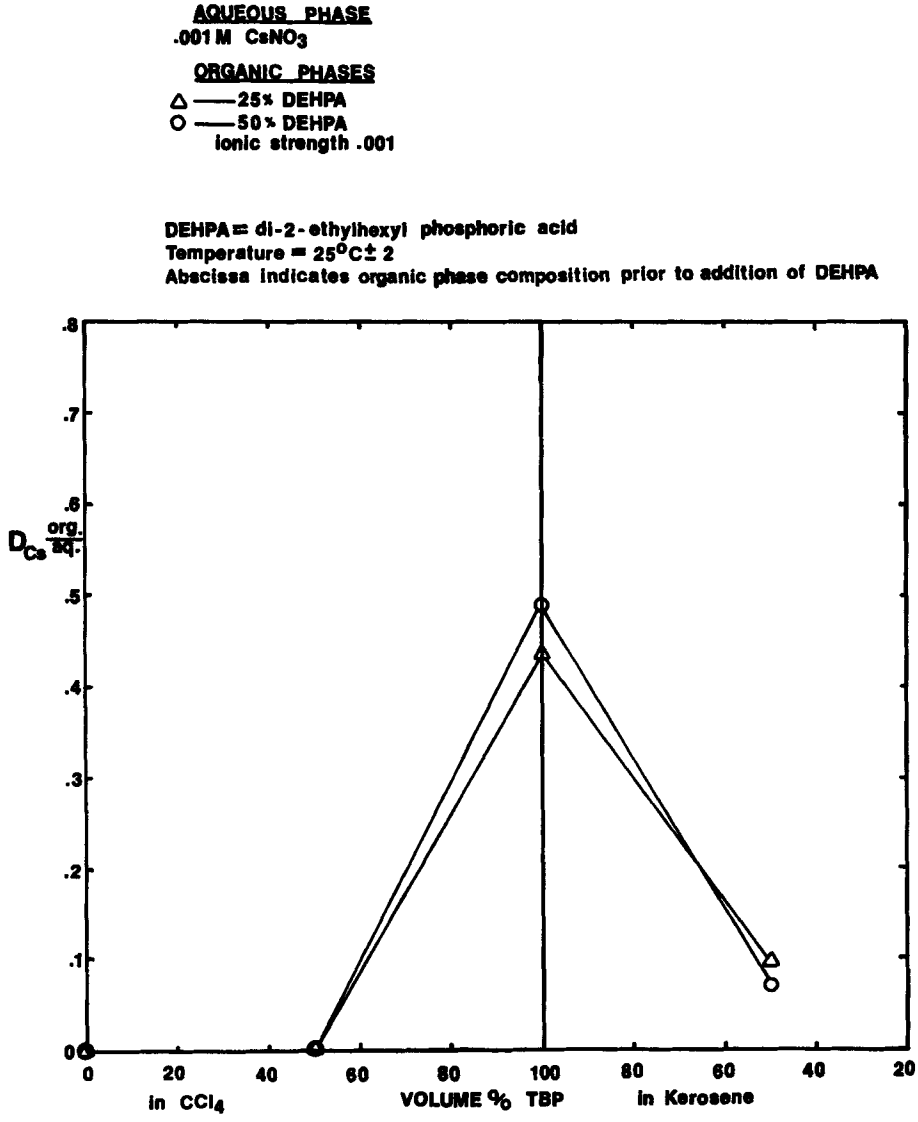

FIG. 8. Distribution of Cs^+ without crown as a function of vol-% TBP and DEHPA.

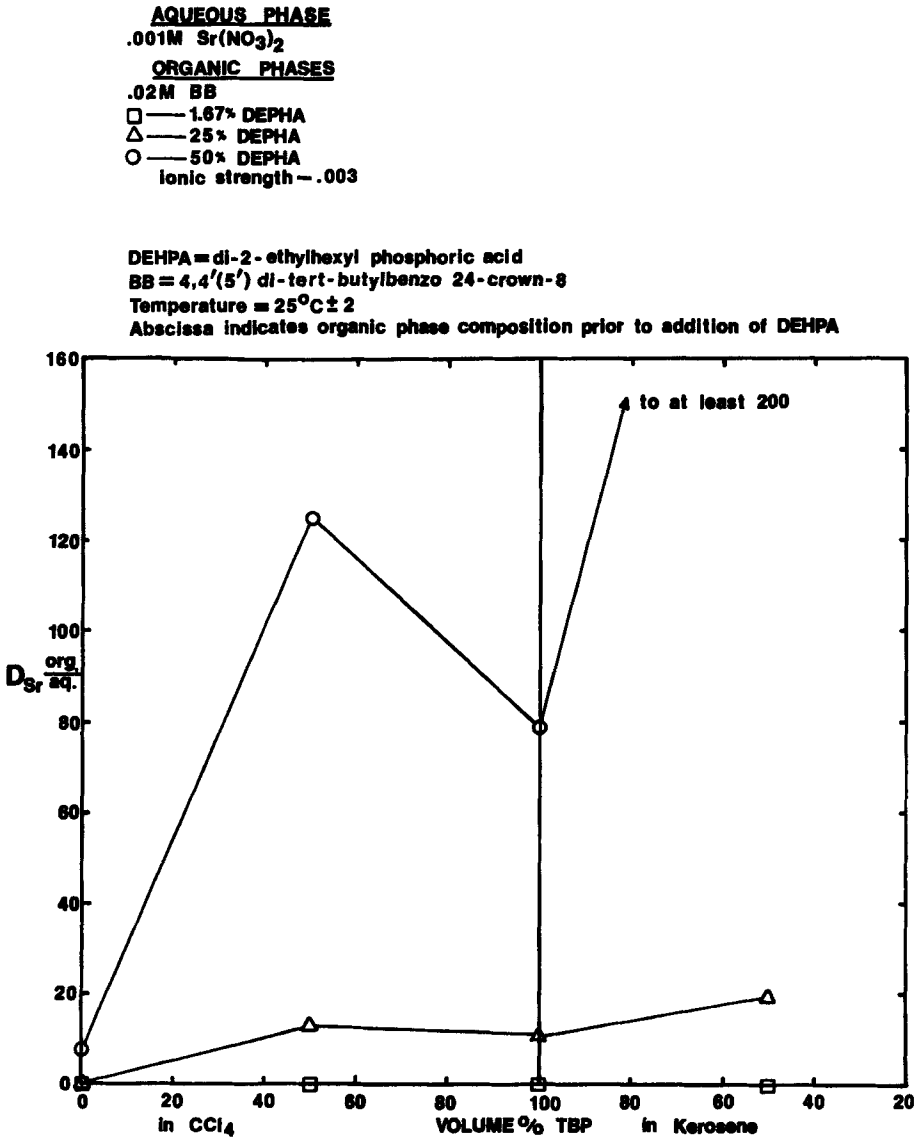

FIG. 9. Distribution of Sr^{2+} with crown as a function of vol-% TBP and DEHPA.

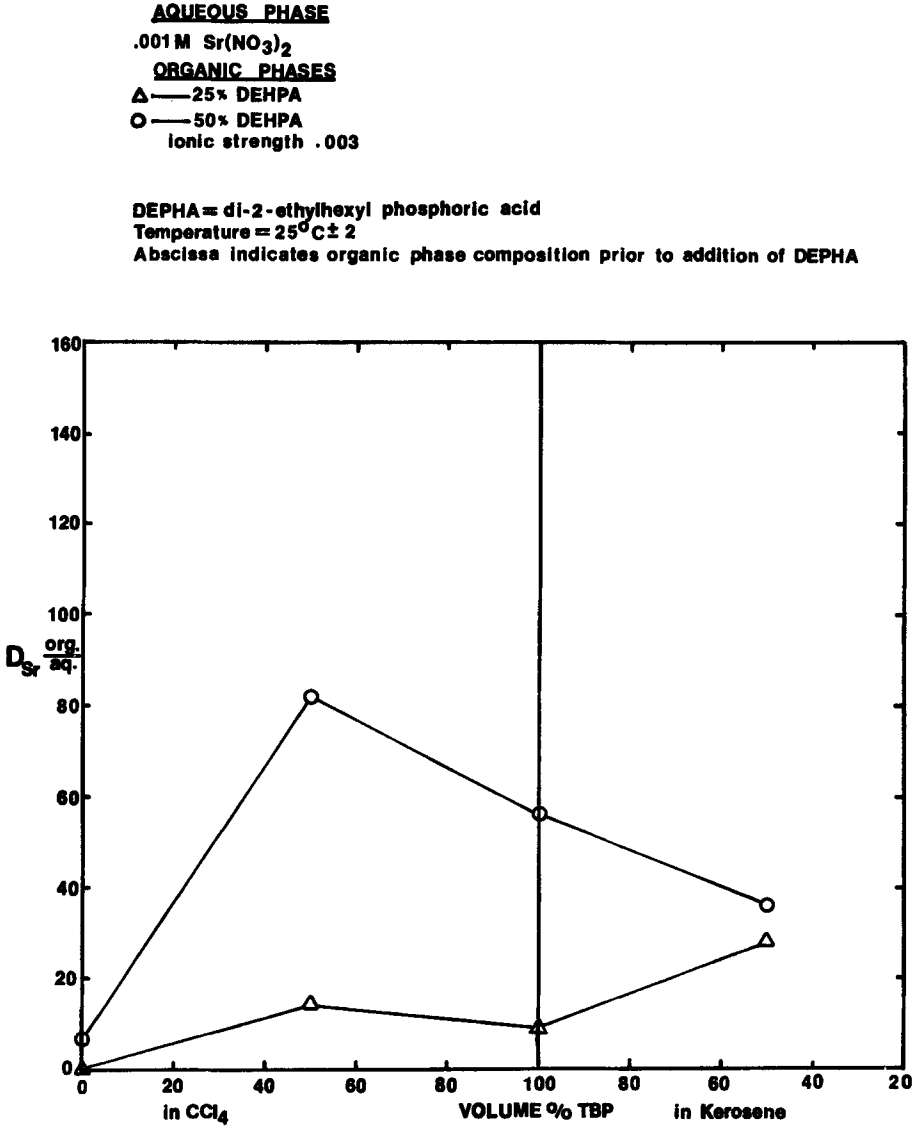

FIG. 10. Distribution of Sr^{2+} without crown as a function of vol-% TBP and DEHPA.

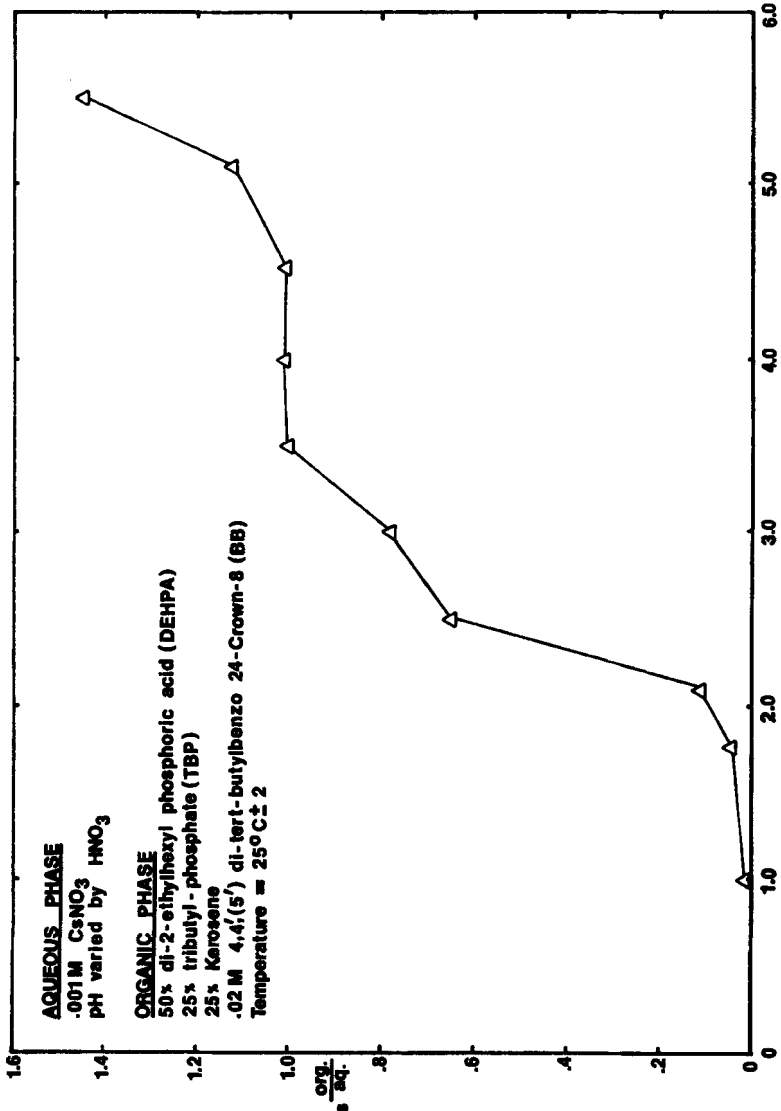

FIG. 11. Distribution of Cs^+ as a function of the aqueous phase pH.

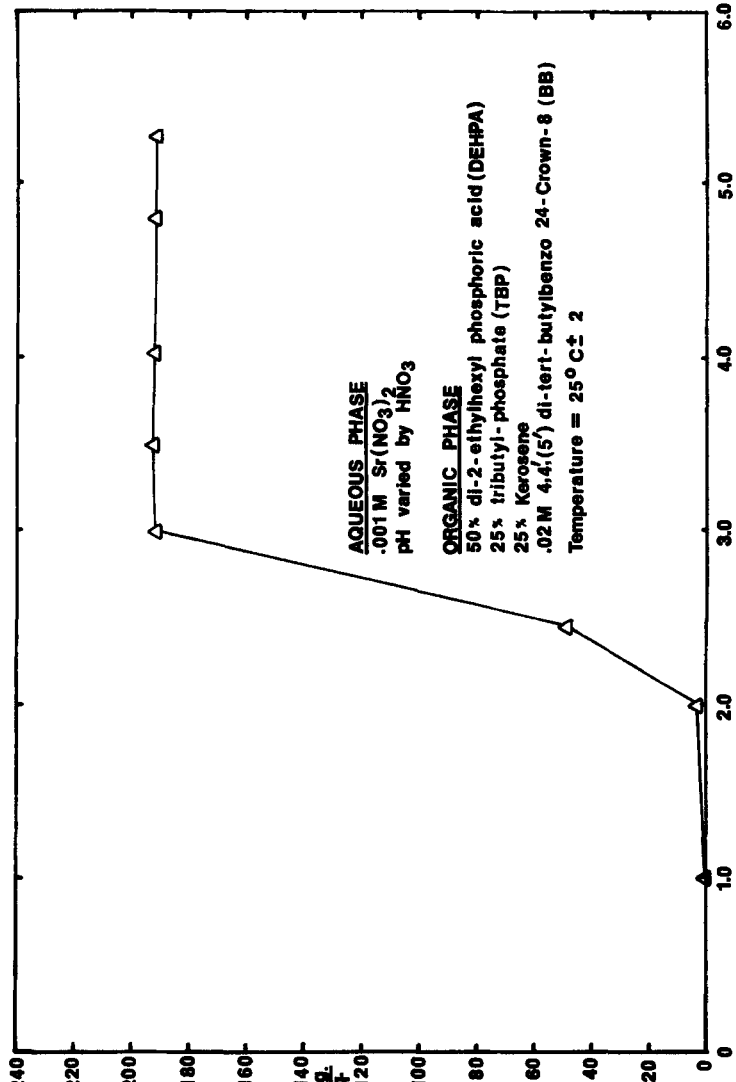

FIG. 12. Distribution of Sr^{2+} as a function of the aqueous phase pH.

Crowns much more soluble in the organic phase will be sought in order to increase the metal carrying capability of the organic phase. Also, a study of the radiation stability of the most promising extraction systems will be undertaken.

At the present time it appears that the single most important factor for the use of crowns in solvent extraction is the necessity of supplying a suitable organic soluble anion to allow transfer of the metal from the aqueous to the organic phase.

Acknowledgment

This research was sponsored by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Washington, D.C. 20545 under Contract No. E (38–1)–884.

REFERENCES

1. C. J. Pedersen, *J. Am. Chem. Soc.*, *89*, 7017 (1967).
2. C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, *2*, 16 (1972).
3. J. J. Christiansen, J. O. Hill, and R. M. Izatt, *Science*, *174*, 459 (1971).
4. C. J. Pedersen, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, *27*, 1305 (1968).
5. H. K. Frensdorff, *J. Am. Chem. Soc.*, *93*, 600 (1971).
6. E. Shchori and J. Jagur-Grodzinski, *Ibid.*, *94*, 7957 (1972).
7. J. J. Christiansen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, pp. 351–384 (May 1974).
8. R. F. Bradley, W. H. Hale, and R. M. Wallace, DP–MS–73–58, Savannah River Laboratory, E. I. du Pont de Nemours, Aiken, South Carolina 29801.

Received by editor August 25, 1978