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Extraction of Cs^+ and Sr^{2+} from HNO_3 Solution Using Macrocyclic Polyethers

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Abstract

A series of crown compounds has been studied in connection with the development of a solvent extraction process for removing Cs^+ and Sr^{2+} from acidic high activity nuclear waste. Crown compounds were investigated because of their ability to form organic soluble complexes with the alkali metals and the alkaline earth metals. The solvent (tributyl phosphate and kerosene) was chosen because of its compatibility with the Purex process currently used at the Savannah River Plant for plutonium and uranium purification. The crown compounds were found not to be sufficiently strong complexing agents to extract these metals from an aqueous phase with an inorganic anion such as nitrate or chloride. However, the use of large organic soluble anions which also functioned as liquid ion exchangers made it possible to extract Cs^+ from 3 *M* HNO_3 while leaving Sr^{2+} and La^{3+} behind. The use of .02 *M* bis-(4,4′(5′)-[1-hydroxyheptyl]-benzo)-18-crown-6 in 0.076 *M* (5 vol-%) didodecylnaphthalene sulfonic acid (DNS)-27 vol-% TBP-68 vol-% kerosene gave the most favorable results for cesium extraction. The two phases separated cleanly and rapidly, yielding a distribution coefficient of 2.0 org/aq from 3 *M* HNO_3. Strontium and lanthanum did not extract significantly at this acid concentration. The distribution data in the low acid region (10^{-4} *M*) are best explained by steric hindrance effects. The lanthanum did not extract at any acid concentration while the strontium extracted very well by a liquid ion-exchange mechanism but the addition of the crown compound did not improve the distribution. The addition of the crown compound improved the Cs^+ distribution markedly in the low acid region even though the Cs^+ diameter is larger than the 18-crown-6-crown cavity while Sr^{2+} should fit very well.

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When the polyether ring is large enough to accommodate the cation (Table 1), the cation is held in the center of the crown by Van der Waals type forces as shown in Fig. 1. If the cation is larger than the crown, other researchers have reported that it may be sandwiched between two crowns (*5*). If the crown is much larger than the cation, the crown may wrap around the cation (*5*, *6*). These references refer to the complex in crystalline form without any side chains and may not apply when the complex is in solutions.

The anion is important in solvent extraction because it must be present in the organic phase if the cation is to be extracted. Although the crown has a partial negative charge in the center due to all the paired electrons of the oxygen atoms pointing toward the center, an anion must be present in the solution with the crown and cation to neutralize the cation.

Since the nitrate (NO_3^-) anion is present in the acidic high activity nuclear waste from the Purex process, it is of interest as a possible inorganic anion. Probably because of its lack of hydrophobic character, however, the NO_3^- anion does not enhance metal extraction into the organic phase. The Cl^- anion is equally ineffective, while the NO_2^- anion is slightly more effective than NO_3^- or Cl^-. The presence of an anion in the organic phase, such as didodecylnaphthalene sulfonic acid (DNS), improves metal

TABLE 1

Ionic and Crown Cavity Diameters

Ionic diameters (Å)[a]	Crown cavity diameters (Å)[b]	
Sr^{2+} 2.26	18-Crown-6	2.6–3.2
Cs^+ 3.38	21-Crown-7	3.4–4.3
	24-Crown-8	>4.0

[a] From Pauling ionic radii (crystalline).

[b] Lower values estimated from Corey-Pauling-Koltum atomic models; higher values from Fisher-Hirschfelder-Taylor models (*2*, p. 20).

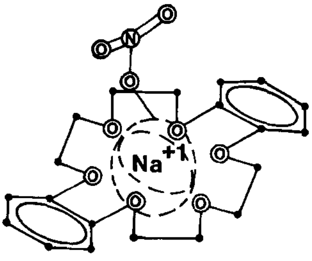

FIGURE 1.

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distribution by lending more organic character to the metal complex. Organic sulfonic and phosphoric acids can be used to supply organic anions because they can exchange their acid proton for the metal at the interface. If steric effects do not prevent it, extraction may occur whether the crown is present or not, but complexation by the crown enhances the extraction by making the complex even more hydrophobic.

The solubility of the crown in both phases is important. If the crown solubility is too large in the aqueous phase, then complexation may take place in the aqueous phase, preventing the metal from being extracted into the organic phase. Maximizing the organic phase solubility while minimizing its aqueous phase solubility will increase the metal-carrying capability of the organic phase and reduce the required flow rates in a solvent extraction process. The addition of large organic side chains to the crown helps insure that they will stay primarily in the organic phase.

In summary, the following parameters have been found important in crown complexation and should be investigated if the crowns are to be used as metal complexing agents in a solvent extraction system (*7*).

(1) The effect of the anion associated with the extracted metal as it contributes to the hydrophobic nature of the complex with large organic anions creating steric effects around the metal which interfere with extraction either by liquid ion exchange alone or with a crown included in the complex.
(2) The effect of the size and nature of the side chains fused to the main polyether ring which strongly affect crown solubility and also affects the hydrophobic nature of the complex and thus its organic phase stability.
(3) The nature and composition of the aqueous and organic phases, including the acid concentration of the aqueous phase and the dipole moments of the various components of the organic phase.
(4) The hydration energies of the ions seem to be important factors affecting their distribution into the organic phase.
(5) The diameter of the crown cavity as compared to the diameter of the ion being extracted seems to be much less important in solvent extraction than previously reported for crystalline complex data.

The structures of the crowns are shown in Fig. 2 and are named with their melting ranges in Table 2. In the subsequent text, the Roman numerals shown with each crown in Fig. 2 and Table 2 will be used to identify the crowns.

The structures of the organic anion suppliers are shown in Fig. 3.

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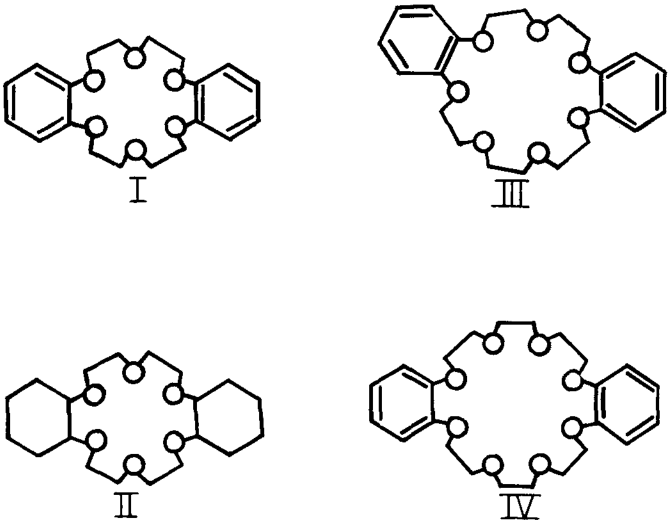

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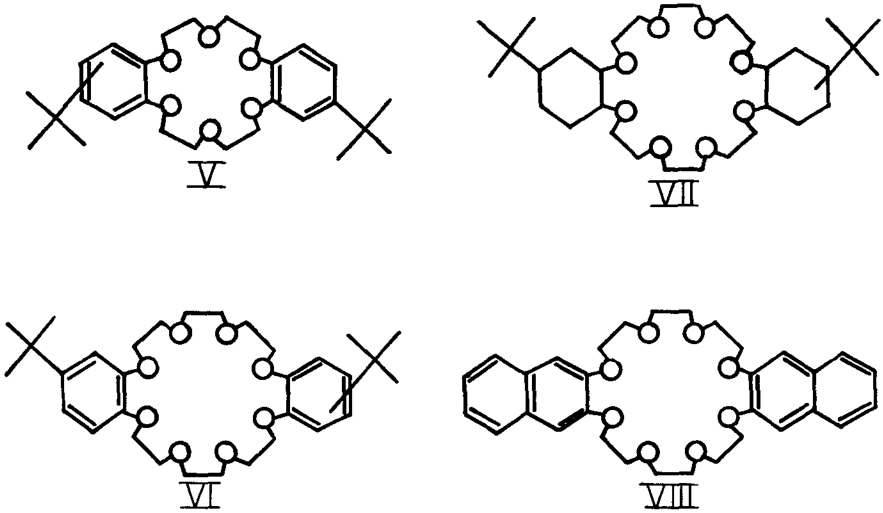

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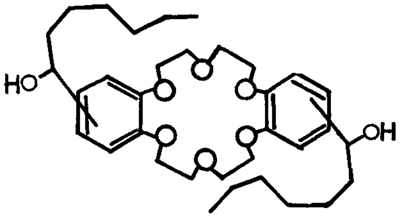

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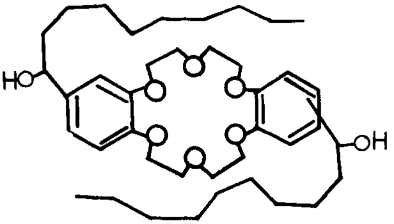

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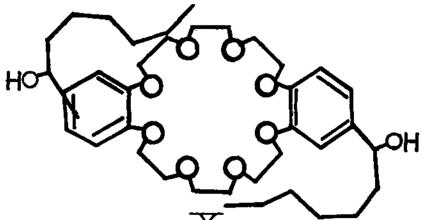

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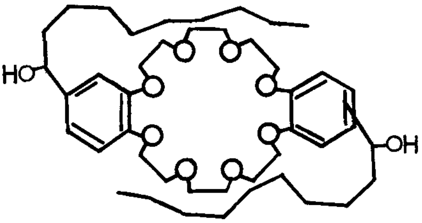

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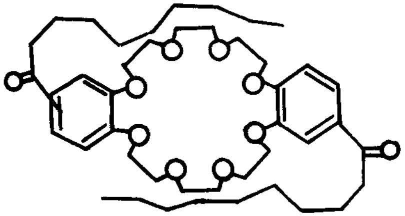
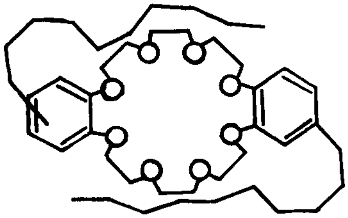
2–(3)



XIII A,B



XIV

2–(4)

FIG. 2. Structures of crowns.

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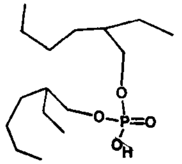
TABLE 2

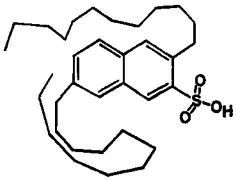
Names, Numbers, Molecular Weights, and Melting Ranges for Structures in Figs. 2 and 3

Number	Name	Molecular weight	Melting range (°C)[a]
I	Dibenzo-18-crown-6	360.4	162–163[b]
II	Dicyclohexo-18-crown-6	368.7	96% pure liquid at 25 °C
III	Dibenzo-21-crown-7	404.5	92–94[b]
IV	Dibenzo-24-crown-8	448.0	103–104
V	4,4′(5′)-Di-tert-butylbenzo-18-crown-6	472.6	118–120[b]
VI	4,4′(5′)-Di-tert-butylbenzo-24-crown-8	560.7	Waxy at 25 °C
VII	4,4′(5′)-Di-tert-butylcyclohexo-24-crown-8	568.6	Liquid at 25 °C
VIII	Di(2′,3′-naphtho)-24-crown-8	548.8	191
IX	Bis-(4,4′(5′)-[1-hydroxyheptyl]-benzo)-18-crown-6	588.8	126–132[b]
X	Bis-(4,4′(5′)-[1-hydroxyheptyl]-benzo)-24-crown-8	676.9	Liquid at 25 °C
XI	Bis-(4,4′(5′)-[1-hydroxydecyl]-benzo)-18-crown-6	673.0	120–135[b]
XII	Bis-(4,4′(5′)-[1-hydroxydecyl]-benzo)-24-crown-8	761.1	90–94
XIIIA	Bis-(4,4′(5′)-decanoylbenzo)-24-crown-8 (less soluble isomer)	757.0	85–95
XIIIB	Bis-(4,4′(5′)-decanoylbenzo)-24-crown-8 (more soluble isomer)	757.0	61–70
XIV	4,4′(5′)-Di-*n*-decylbenzo-24-crown-8	731.1	62–73
XV	Di-2-ethylhexyl phosphoric acid (DEHPA)	322.4	Liquid at 25 °C
XVI	Didodecylnaphthalene sulfonic acid (DNS)	563.6	Liquid at 25 °C

[a] Melting ranges for Crowns V-VII and IX-XIV reflect a mixture of isomers.
[b] Reported by Parish Chemical Co.



DEHPA
XV



XVI, DNS

FIG. 3. Structures of organic soluble anion suppliers.

EXPERIMENTAL

Apparatus, Chemicals, and Procedures

Samples were shaken at 330 oscillations/min on a wrist-action shaker manufactured by Burrell Corp., Pittsburgh, Pennsylvania.

The metal concentration in the aqueous phase was determined using a Jarrell-Ash Model 530 Atomic Absorption Spectrophotometer by absorption for Sr^{2+} and by emission for Cs^+.

The organic concentration in the various aqueous phases was analyzed using a Beckman Model 915A Total Carbon Analyzer (TCA).

The pH of the aqueous phases was determined by using a Corning pH Meter Model 10. Acid concentrations greater than 0.1 *M* (pH 1.0) were titrated with dilute NaOH solution using phenolphthalein as an indicator. The pH buffer standards were obtained from Fisher Scientific Co., Fairlawn, New Jersey, as were the concentrated acids.

The dicyclohexo-18-crown-6 (II) was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. The dibenzo-24-crown-8 (IV) and the di-(2′,3′-naphtho)-24-crown-8 (VIII) were synthesized at the University of South Carolina, by the method described by Pedersen (*15*). The rest of the crowns (I, III, V–VII, IX–XIV) were synthesized by Parish Chemical Co., Provo, Utah.

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The di-2-ethylhexyl phosphoric acid (XVI, DEHPA) was obtained from Mobil Chemical Co., Charleston, South Carolina. Because it contained 2–3% mono-2-ethylhexyl phosphoric acid, the DEHPA was purified by the method described by McDowell et al. (*16*). The didodecylnaphthalene sulfonic acid (XVII, DNS) (*17*) was obtained from King Industries, Norwalk, Connecticut, as 50% active DNS in Norpar 12 [a mixture of normal paraffins (C_{11}–C_{13})]. No indication of the purity could be obtained from King Industries.

The TBP was obtained from both Matheson Coleman and Bell of Norwood, Ohio, and Fisher Scientific. It was purified by the method outlined by Irving and Edgington (*18*).

The kerosene was a mixture of normal paraffins (C_{12} 9.5%, C_{13} 55.1%, C_{14} 35.3%, and C_{15} 0.1%) obtained from the Continental Oil Co., Baltimore, Maryland. This is the same kerosene used by the Savannah River Plant, Aiken, South Carolina, in their Purex solvent extraction process. The kerosene was used without futher purification.

The metals were obtained from the following companies: Fisher Scientific, Pfaltz and Bauer, and Allied Chemical. The stock solutions of these metals were prepared by dissolution of weighed amounts of the salts in previously prepared nitric acid solutions.

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Procedure

Aqueous phases tested were composed of various HNO_3 concentrations ranging from 3×10^{-6} to 3 *M* and containing 0.01 *M* $CsNO_3$, $Sr(NO_3)_2$, and $La(NO_3)_3$.

Organic phases tested were composed of an individual crown dissolved in kerosene with varying concentrations of TBP. In some tests as much as 35 vol-% DEHPA or 5 vol-% DNS was also added to the organic to furnish organic anions.

Aqueous samples were shaken for 1 h with equal volumes of organic phase containing various crowns and other complexing agents such as TBP. All experimental data were obtained at 25 ± 2°C. The metal content of the aqueous phase was analyzed using the Atomic Absorption Spectrophotometer (AA). The difference between the aqueous phase concentrations of the samples shaken and the original metal concentration was interpreted as the amount of metal complexed by the extractants in the organic phase. The organic samples were shaken with equal volumes of fresh aqueous phase to back extract the metal in order to check the total material balance. At least two back extractions were normally necessary to remove the Cs^+ from the organic phase. The material balances agreed within ±10%. These back extractions showed that the metals could be back extracted reversibly. The reversibility was shown to be true in all systems studied no matter how large the distribution coefficient. Due to limitations of the spectrophotometer, no distributions above 193, which is 99.5% removal, are reported.

Solubilities of the crowns in organic phases were determined by adding small increments of the organic phase to a known amount of crown and shaking up to 2 h between additions of organic until the crown dissolved. Most solubilities measurements were checked at least twice.

Solubilities of the crowns in various aqueous phases were determined by equilibrating the crown alone with the aqueous phase in question. The crown solubility was calculated knowing the crown structure and data obtained from the Total Carbon Analyzer (TCA). The solubility data were reproducible to within ±5%.

Distribution data for the crowns between the organic and aqueous phases were determined by equilibrating the aqueous phase with the organic solvent containing the crown. A reference solvent solubility was obtained by equilibrating an identical aqueous phase with the organic solvent alone. Both samples were analyzed using TCA. The difference in the ppm of CO_2 between the two samples was interpreted as being due to the crown concentration. Since this technique often required subtracting two large numbers, the data were less accurate than the direct solubility determination. In general, less crown was found in the aqueous phase in the distribution experiments than would have been indicated by aqueous phase solubility measurements made with no organic phase present.

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THEORY

Extraction Models

There are least three extraction models which allow an explanation of the data for the extraction of Cs^+ and Sr^{2+}. These models are:

(1) Extraction with crown and organic anion supplier
(2) Extraction with organic anion supplier only
(3) Extraction with crown, organic anion supplier, and NO_3^-

Extraction with Crown and Organic Anion Supplier

The first model is one in which both the crown compound and the organic anion supplier are involved in the extraction:

$$M_{aq}^{n+} + nROH_{(org)} + m\,\text{crown}_{org} \overset{K_{eq}}{\rightleftharpoons} [M\text{-}(OR)_n(\text{crown})_m]_{org} + nH_{aq}^+ \tag{1}$$

where ROH = any anion supplier (DNS or DEHPA)
M = metal cation (Cs^+ or Sr^{2+})
m = number of crown molecules in complexes
n = charge on the metal ion
org = organic
aq = aqueous

It can be seen from the above equation that the aqueous acid concentration plays an important role in the distribution of the metal into the organic phase. The organic anion suppliers shed a proton into the aqueous phase in order to pick up the metal ion. It is expected that this exchange would take place at the phase interface.

At equilibrium, the equilibrium constant, K_{eq}, is

$$K_{\text{eq}} = \frac{(a_{\text{complex}})_{\text{org}}(a_{\text{H}^+})_{\text{aq}}{}^n}{(a_{\text{crown}})^m_{\text{org}}(a_{\text{metal}})_{\text{aq}}(a_{\text{ROH}})^n_{\text{org}}} \tag{2}$$

where a_i is the activity of the ith species.

The activity is defined in the following manner:

$$a_i = (\gamma_i)[i] \tag{3}$$

where γ_i = activity coefficient of the ith species
$[i]$ = concentration of the ith species

Thus K_{eq} becomes

$$K_{\text{eq}} = \frac{(\gamma_{\text{complex}})_{\text{org}}[\text{complex}]_{\text{org}}(\gamma_{\text{H}^+})_{\text{aq}}{}^n[\text{H}^+]_{\text{aq}}{}^n}{(\gamma_{\text{crown}})^m_{\text{org}}[\text{crown}]^m_{\text{org}}(\gamma_{\text{metal}})_{\text{aq}}[\text{metal}]_{\text{aq}}(\gamma_{\text{ROH}})^n_{\text{org}}[\text{ROH}]^n_{\text{org}}} \tag{4}$$

The distribution coefficient, $D_{\text{org/aq}}$, for the metal between the two phases is

$$D_{\text{org/aq}} = \frac{[\text{complex}]_{\text{org}}}{[\text{metal}]_{\text{aq}}} \tag{5}$$

By substituting $D_{\text{org/aq}}$ into Eq. (4), the expression for K_{eq} becomes

$$K_{\text{eq}} = \frac{(\gamma_{\text{complex}})_{\text{org}}D_{\text{org/aq}}(\gamma_{\text{H}^+})_{\text{aq}}{}^n[\text{H}^+]_{\text{aq}}{}^n}{(\gamma_{\text{crown}})^m_{\text{org}}[\text{crown}]^m_{\text{org}}(\gamma_{\text{metal}})_{\text{aq}}(\gamma_{\text{ROH}})_{\text{org}}[\text{ROH}]^n_{\text{org}}} \tag{6}$$

Since the data taken during this research do not lend themselves well to determining the individual organic activity coefficients, this equilibrium equation can be reduced no further. By rearranging the equation, it is possible to see the effect of the various species on the $D_{\text{org/aq}}$.

$$D_{\text{org/aq}} = \frac{K_{\text{eq}}(\gamma_{\text{crown}})^m_{\text{org}}[\text{crown}]^m_{\text{org}}(\gamma_{\text{metal}})_{\text{aq}}(\gamma_{\text{ROH}})^n_{\text{org}}[\text{ROH}]^n_{\text{org}}}{(\gamma_{\text{complex}})_{\text{org}}(\gamma_{\text{H}^+})_{\text{aq}}{}^n[\text{H}^+]_{\text{aq}}{}^n} \tag{7}$$

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An examination of Eq. (7) shows that the organic phase activity coefficients of the metal complex as well as those of the complexing agents must be known to calculate the distribution coefficient. Sufficient data are not available to make these calculations. However, it is possible to make an approximation of the relative values of K_{eq} for Cs^+ and Sr^{2+}.

By assuming that the K_{eq} is principally a function of the standard free energies of solvation of the ions in question, an explanation may be found in a paper by Hedwig et al. (*8*):

> The standard free energies of solvation (gas phase to liquid phase) of divalent cations in polar solvents are usually much more negative than those for monovalent cations. ($\Delta G_{solvation}$ (M^{2+}) typically −1000 to −2000 kJ/g-ion; $\Delta G_{solvation}$ (M^{+1}) typically −250 to −500 kJ/g-ion.) Compared with monovalent cations, divalent cations generally are smaller and have a greater charge density. They are thus expected to interact more strongly with and to cause more extensive structuring of polar solvents within ion-centered solvation shells than do monovalent cations.

Applied to the present work, this implies that the values of the K_{eq} for Cs^+ should be greater than for Sr^{2+}. In other words, Cs^+ should extract more readily into the organic phase. More work concerning hydration energies is discussed by Rosseinsky (*9*).

Data on hydration energies of all Group I ions are shown in Table 3 from Cotton and Wilkinson (*10*).

Recent experiments show that Rb^+ does not extract as well as Cs^+ into the organic with Crown IX and DNS in 27% TBP–68% kerosene. Since the crystal radii would indicate that Rb^+ would fit better into any 18-crown-6 than Cs^+, observed extraction results may be due to the higher hydration energy of Rb^+ as shown in Table 3 or to the possibility that the forms of the two complexes are different, i.e., Cs^+ may be sandwiched between two crowns while Rb^+ may complex with only one crown, thus decreasing its organic solubility.

TABLE 3

Data on Hydration of Aqueous Group I Ions

	Li^+	Na^+	K^+	Rb^+	Cs^+
Crystal radii[a], Å	0.86	1.12	1.44	1.58	1.84
Hydrated radii (approx), Å	3.40	2.76	2.32	2.28	2.28
Approximate hydration numbers[b]	25.3	16.6	10.5	—	9.9
Hydration energies, kJ/mol	519	406	322	293	264
Ionic mobilities (at infinite dilution) (*18*)	33.5	43.5	64.6	67.5	68

[a] Ladd radii.

[b] From transference data.

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Extraction with Organic Anion Supplier Only

The second extraction model consists of liquid ion exchange alone, involving only the organic anion supplier (organic acid). Using the nomenclature from Eq. (1), the equation becomes

$$M_{aq}^{n+} + nROH_{(org)} \overset{K_{eq'}}{\rightleftharpoons} [M-(OR)_n]_{org} + nH_{aq}^{+} \tag{8}$$

At equilibrium, the equilibrium constant, $K_{eq'}$, is

$$K_{eq'} = \frac{(a_{complex})_{org}(a_{H^+})_{aq}^{n}}{(a_{metal})_{aq}(a_{ROH})_{aq}^{n}} \tag{9}$$

Substituting for the activity as in Eq. 4,

$$K_{eq'} = \frac{(\gamma_{complex})_{org}[complex]_{org}(\gamma_{H^+})_{aq}^{n}(H^+)_{aq}^{n}}{(\gamma_{metal})_{aq}[metal]_{aq}(\gamma_{ROH})_{org}^{n}[ROH]_{org}^{n}} \tag{10}$$

Substituting Eq. (5) into Eq. (10) and rearranging,

$$D_{org/aq} = \frac{K_{eq'}(\gamma_{metal})_{aq}(\gamma_{ROH})_{org}^{n}[ROH]_{org}^{n}}{(\gamma_{complex})_{org}(\gamma_{H^+})_{aq}^{n}[H^+]_{aq}^{n}} \tag{11}$$

As before, the $K_{eq'}$ for Cs^+ should be greater than that for Sr^{2+}. As in the first model, the expression for the distribution coefficient contains a group of organic phase activity coefficients which cannot be evaluated numerically. The value of γ_{ROH} is assumed approximately equal for both models. However, the value for $\gamma_{complex}$ should be different in the second model, and the γ_{crown} does not appear at all in the second model.

Extraction with Crown, Organic Anion Supplier, and NO_3^-

A third model is one in which the crown complexation is so strong (for example, Cs^+ in a sandwich of two crowns) that the hydrophobic nature of the complex is sufficient to support NO_3^- ion in the organic phase. In a similar manner, Sr^{2+} might have its valance satisfied by an organic anion coupled with NO_3^- ion provided the combination of one or more crowns and an organic acid anion gave it sufficient hydrophobic character. This phenomenon has been observed in the rare earth extraction by TBP and thenoyltrifluoroacetone (HTTA) in a kerosene diluent where the form of the complex is $M(TBP)_2(TTA)_2NO_3$ (*11*, *12*).

Side Effects

There are several other effects which influence the metal distribution coefficient. These are listed below.

(1) The acid concentration affects the complexation of the metal by the crown in the following ways:
   (a) Some of the acid dissolved in the organic phase complexes with the TBP (*13*):

$$\mathrm{TBP} + \mathrm{HNO_3} \rightleftarrows \mathrm{TBP \cdot HNO_3} \tag{12}$$

   The dissolved acid should help support the charge separation of the crown complex, increasing the metal's organic solubility.
   (b) Extraction of acid into the organic phase lowers the acid concentration in the aqueous phase. This decrease in ionic strength changes the activity coefficients of both the metal and the H^+, altering the value of the distribution coefficient (see Eq. 7).
   (c) The acid dissolved in the organic phase may protonate the crown, thus reducing its availability for complexation.
   (d) From Eqs. (7) and (11) it is apparent that increasing the charge on the metal ion (n) will either raise or lower the $D_{\mathrm{org/aq}}$, depending on the ionic strength of the aqueous phase (see Fig. 4).

(2) Since both DNS and DEHPA are large organic molecules, they are hydrophobic. The DNS, being a much larger molecule (see Fig. 3), lends more hydrophobic character to the complex and should increase the metal extraction.

(3) The DNS being a stronger acid than the DEHPA has more ionized molecules at any given acid concentration.

(4) Steric effects are created by the large DNS molecules coupled with the long side chains of some of the crowns (see Figs. 14 through 16). These steric effects apparently prevent complexation by the crown for Sr^{2+}, thus decreasing $D_{\mathrm{org/aq}}$.

Isometric representations of some of the metal-crown complexes with the organic anions are shown in Figs. 14 though 16.

The Extended Debye-Huckel Theory of Strong Electrolytes

The aqueous activity coefficients, γ_{metal} and $\gamma_{\mathrm{H^+}}$, can be calculated from the extended Debye-Huckel theory of strong electrolytes (14):

$$-\log \gamma_i = \frac{Az^2 I}{1 + Ba_i I} - bI \tag{13}$$

where γ_i = activity coefficient of the ith species
A, B, b = constants 0.5115, 0.3291, and 0.2, respectively

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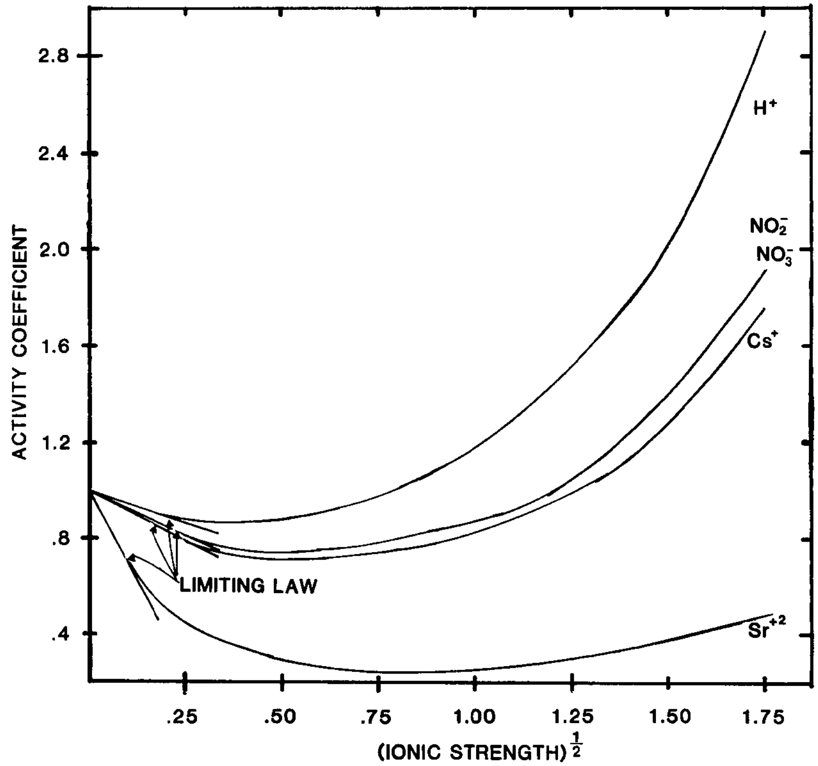

FIG. 4. Theoretical curves from extended Debye-Huckel theory of strong electrolytes for H^+, NO_3^-, NO_2^-, Cs^+, and Sr^{2+}.

z_i = charge of the ith species
a_i = effective hydrated radius of the ith species:
$Cs^+ = 2.5$
$Sr^{2+} = 5.0$
$H^+ = 9.0$
I = ionic strength

The constants (A, B, b) do not contain any interaction parameters which take into account the molecular interactions which exist at higher acid concentrations. The equations utilizing the interaction parameters are very cumbersome and contribute little to an understanding of the general trends of these coefficients. In Fig. 4 (derived from Eq. 13), it can be seen that as the ionic strength increases, the activity coefficients deviate considerably from unity (their value at infinite dilution). The actual numerical values of the activity coefficients are strongly dependent on the ionic strength.

ANALYSIS OF DATA

Solubility

Organic Crown Solubility in TBP-Kerosene

Compatibility with the Purex process was a major consideration in the solvent choice. The organic solvents used in testing the solubility of the crowns were kerosene with varying TBP concentrations as shown in Table 4. The solubilities for many of the crowns were significantly higher in pure CCl_4 than in any of the combinations with TBP tested (Table 4).

When the tert-butyl groups were added to each of the benzene rings of a dibenzo crown, e.g., converting dibenzo-24-crown-8 (IV) to 4,4′(5′)-di-tert-butylbenzo-24-crown-8 (VI), the organic solubility increased 4-fold in 50% TBP–kerosene. The conversion of dibenzo-18-crown-6 (I) to 4,4′(5′)-di-tert-butylbenzo-18-crown-6 (V) resulted in a solubility increase of about 280-fold in 50% TBP–kerosene. For these same crowns the solubility in 0.10 *M* HNO_3 decreased (Table 5). Hydrogenating the two benzene rings attached to the polyether ring, e.g., converting di-tert-

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TABLE 4

Solubility of the Crowns in the Organic Solvents

Crown	Solubility (mol/L)			
	50% TBP-Kerosene	TBP	CCl_4	Other
I	0.00050	0.00135	0.0291	
II		0.075	0.310	0.050 3.1% TBP-kerosene
III	0.00494	0.0110	0.0567	
IV	0.006	0.0130	0.020	0.00064 3.1% TBP-kerosene
V	0.140	0.180	0.622	
VI	0.0229	0.0310	0.050	0.0037 3.1% TBP-kerosene
VII		0.360	1.18	0.070 5% TBP-kerosene
VIII			0.00009	0.654 CCl_3H
IX	0.0284	0.0629	0.00158	
X	0.0241	0.0446	0.220	
XI	0.0021	0.0064	0.0011	
XII	0.0015	0.0085	0.0004	
XIIIA	0.003	0.0019	0.0072	
XIIIB	0.0096	0.0039	0.0025	
XIV	0.0039	0.0049	0.0178	

TABLE 5

Solubility of Crowns and Organic Soluble Anion Suppliers in Aqueous Phases

	Solubility (mol/L)				
Crown	0.10 *M* HNO_3	2.0 *M* HNO_3	1.5 *M* $CsNO_3$	2.0 *M* $Sr(NO_3)_2$	3.16×10^{-6} *M* HNO_3
I	0.000255	0.000558	0.000451	0.000139	0.000305
II	0.022				
III	0.00057	0.00063	0.00217	0.000487	0.000496
IV	0.00035	0.00172	0.00156	0.000303	0.000134
V	0.000233	0.000393	0.000222	0.000114	0.000374
VI	0.000086	0.0054	0.00173	0.000825	0.000241
VII	0.00097	0.0064	0.00527	0.00401	0.000130
VIII	0.00009	0.00079	0.000129	0.000133	0.0000202
IX	0.00000846	0.0000374	0.0000236	0.0000921	0.0000072
X	0.0000943	0.0000943	0.0000301	0.0000341	0.0000606
XI	0.0000317	0.0000317	0.0000337	0.0000317	0.0000207
XII	0.00018	0.00018	0.000173	0.000087	0.0000312
XIIIA	0.000036	0.00044	0.00077	0.000053	0.0000180
XIIIB	0.00017	0.00048	0.000077	0.000044	0.000061
		Organic Soluble Anion Supplier			
XV	0.00028	0.00093	0.00012	0.00020	0.00022
XVI	0.000284	0.000305	0.00020	0.000116	0.00039

butylbenzo-24-crown-8 (VI) to 4,4′(5′)-di-tert-butylcyclohexo-24-crown-8 (VIII), increased the organic solubility in 100% TBP by a factor of 11 (Table 4) as well as increasing the solubility in 0.10 *M* HNO_3 by a similar factor (Table 5).

In order to maximize the organic solubility and minimize the aqueous solubility, the chain length on the benzene rings in the dibenzo crowns was increased to a single straight 7- or 10-membered chain on each benzene ring. The effect of chain length on organic solubility is shown in Fig. 5. The optimum chain length for maximum organic solubility appeared to be between 4 and 7. Branched chains containing the same number of carbons are in general much more soluble in the organic phase than their straight chain equivalents. Increasing the chain length on the cyclohexane rings to 7 or 10 carbons may substantially increase the organic solubility without the large increase in the aqueous solubility that occurred with Crown VII. The organic solubility increased regularly as the crown size increased (dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8) in 50% TBP–kerosene.

Aqueous Crown Solubility

The solubilities of the crowns were determined in 3.16×10^{-6}, 0.10,

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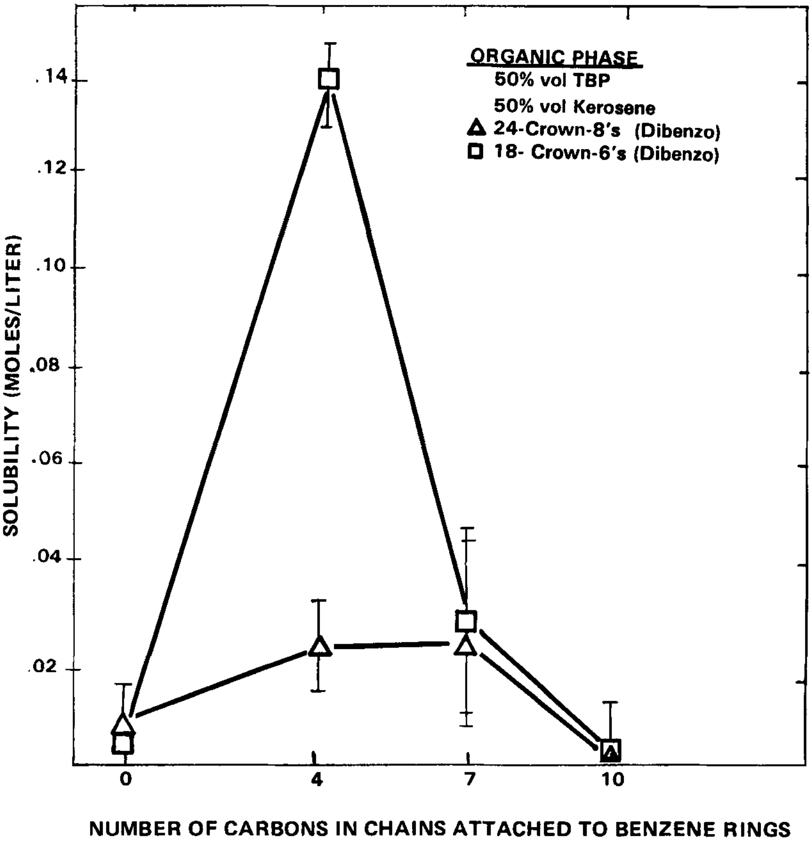

FIG. 5. Organic solubility of crowns with varying chain length in 50% TBP–kerosene.

and 2.0 *M* HNO_3 (Table 5). The highest acid concentration was approximately the same as the acidity of the high activity nuclear waste from the Purex process.

The generally higher solubility of the crowns in 2.0 *M* HNO_3 is believed to be due to the increased concentration of protons available to hydrogen bond with the oxygens in the polyether ring. Also shown in Table 5 are the solubilities of the crowns in solutions of 1.5 *M* $CsNO_3$ (saturated) and in 2.0 *M* $Sr(NO_3)_2$. One element of interest here is the high solubility of the dibenzo-21-crown-7 (III) in $CsNO_3$ solution. This is not totally unexpected since its cavity is the right size for the Cs^+ to fit comfortably (Table 1). Unfortunately, this crown is very expensive because of its asymmetry and, therefore, is of doubtful use for plant-scale processing.

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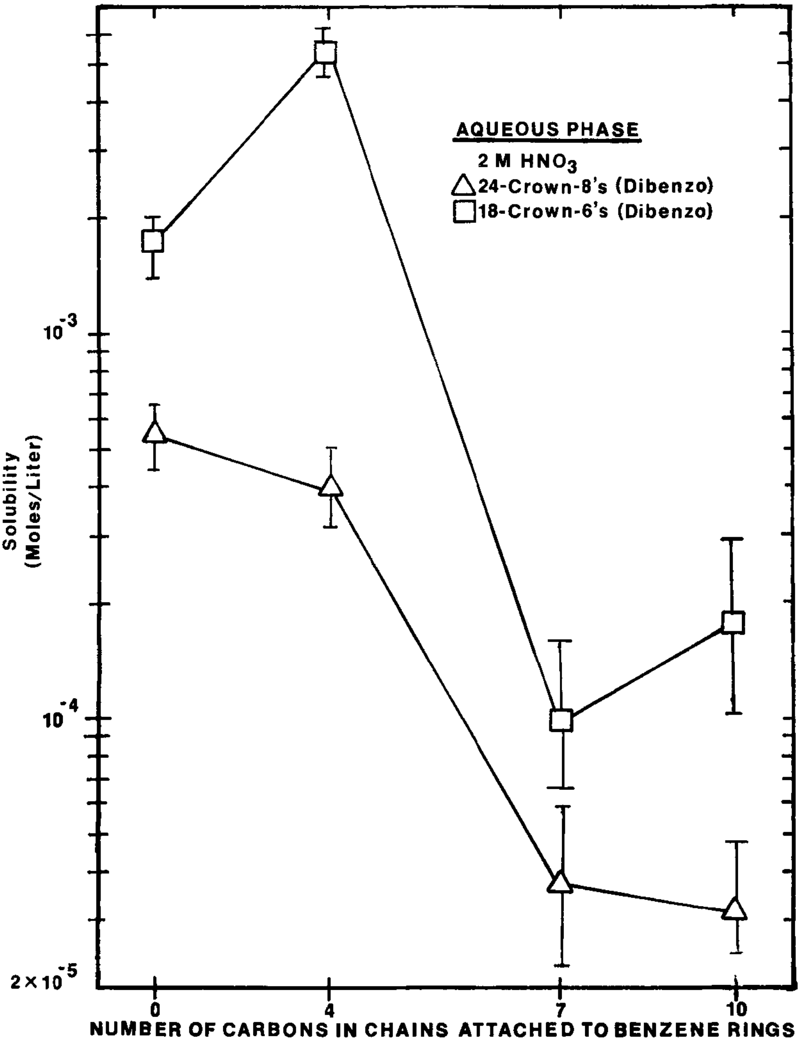

FIG. 6. Aqueous solubility of crowns with varying chain length in 2 *M* HNO_3.

The effect of chain length on the aqueous solubility is shown in Fig. 6. A sharp drop in the aqueous solubility appeared for crowns having 4- to 7-membered chains. A low aqueous solubility would decrease the complexation of the metal in the aqueous phase and minimize the loss of expensive crown during processing. As previously noted, optimum organic solubilities of the crowns occur for those with 4- and 7-membered chains with branched chains giving appreciably greater solubility.

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Inorganic Anions

The distribution of Cs^+ and Sr^{2+} into TBP-kerosene and TBP-CCl_4 mixtures was studied using three inorganic anions: NO_3^-, NO_2^-, and Cl^-. All of the distribution coefficients were too small to be useful in a solvent extraction system. The highest $D_{org/aq}$ was 0.14 with an HNO_3 con-

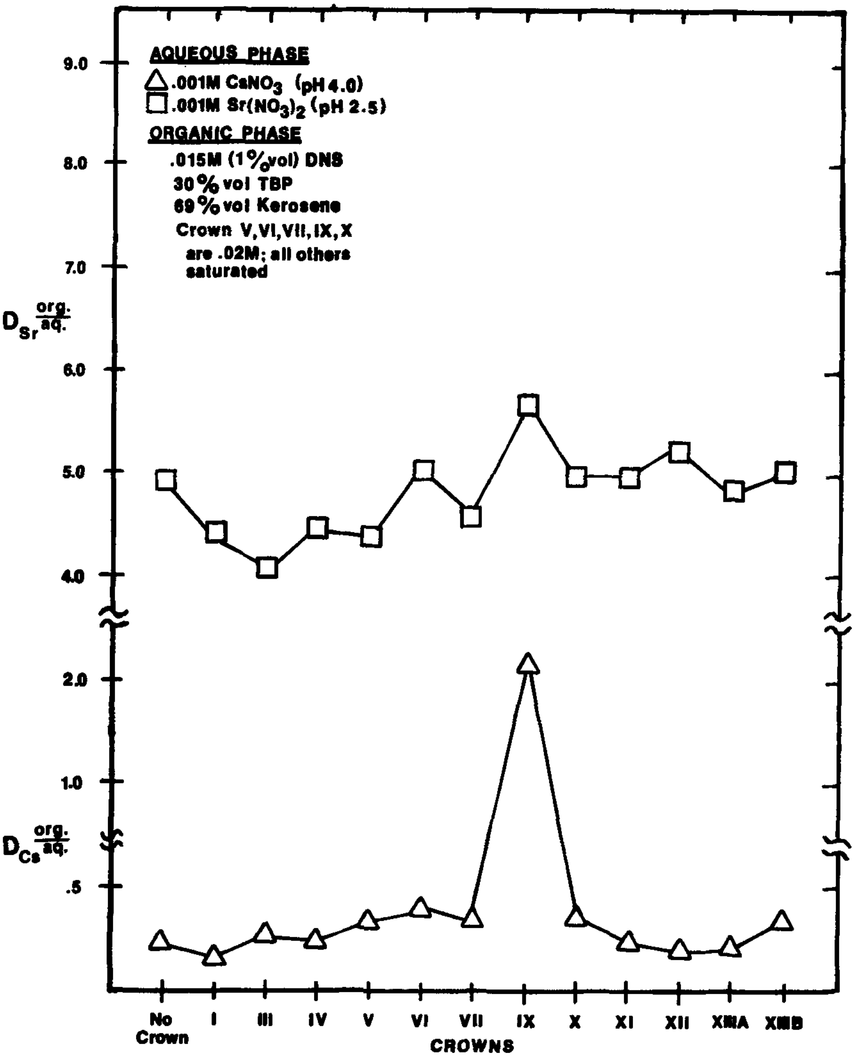

FIG. 7. Cesium and strontium distribution with various crowns in 1% DNS–30% TBP-kerosene.

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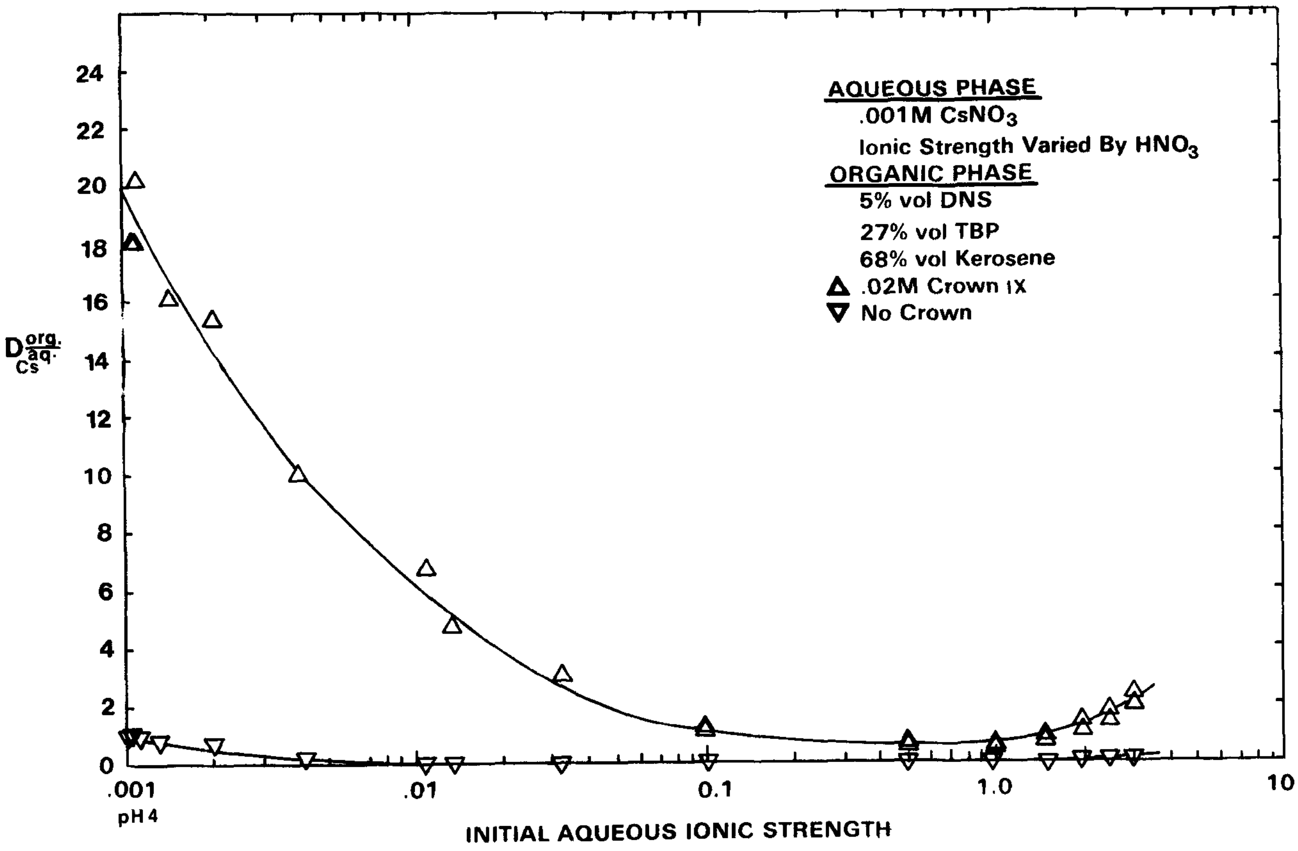

FIG. 8. Cesium distribution with Crown IX in 5% DNS–27% TBP–kerosene.

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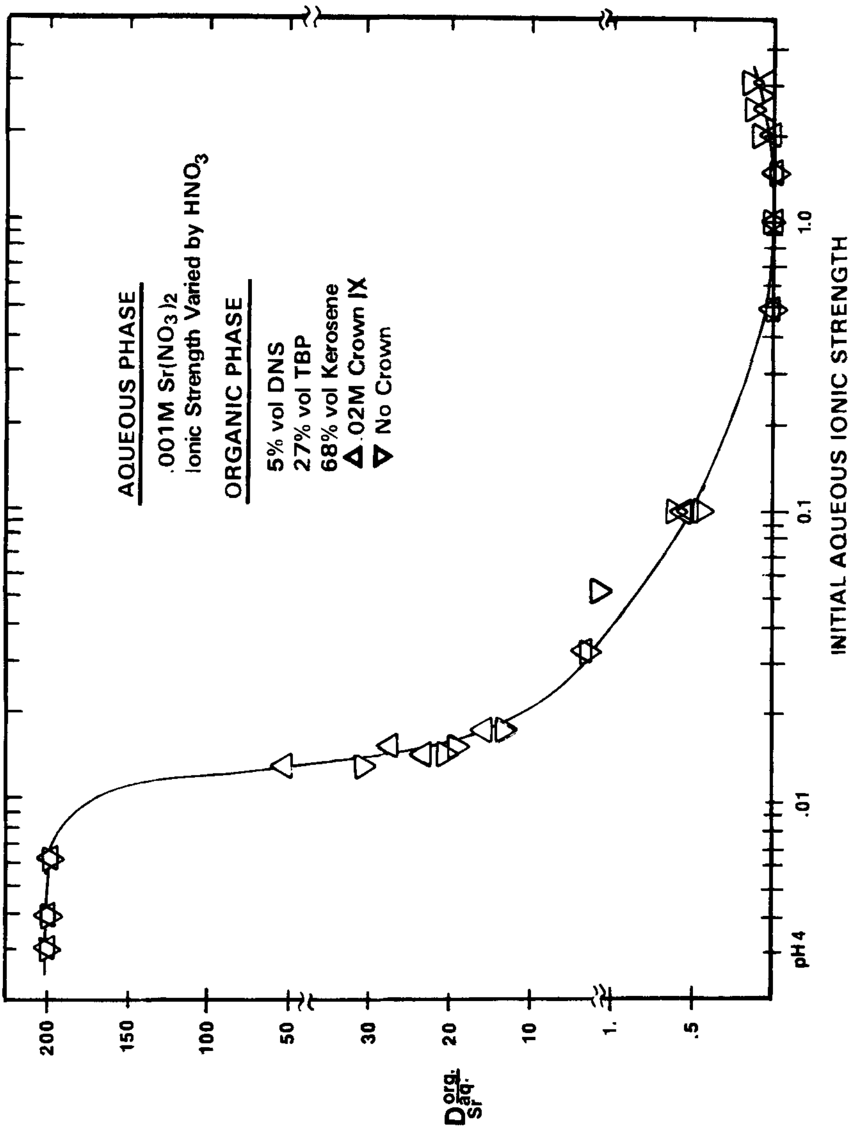

FIG. 9. Strontium distribution with Crown IX in 5% DNS–27% TBP–kerosene.

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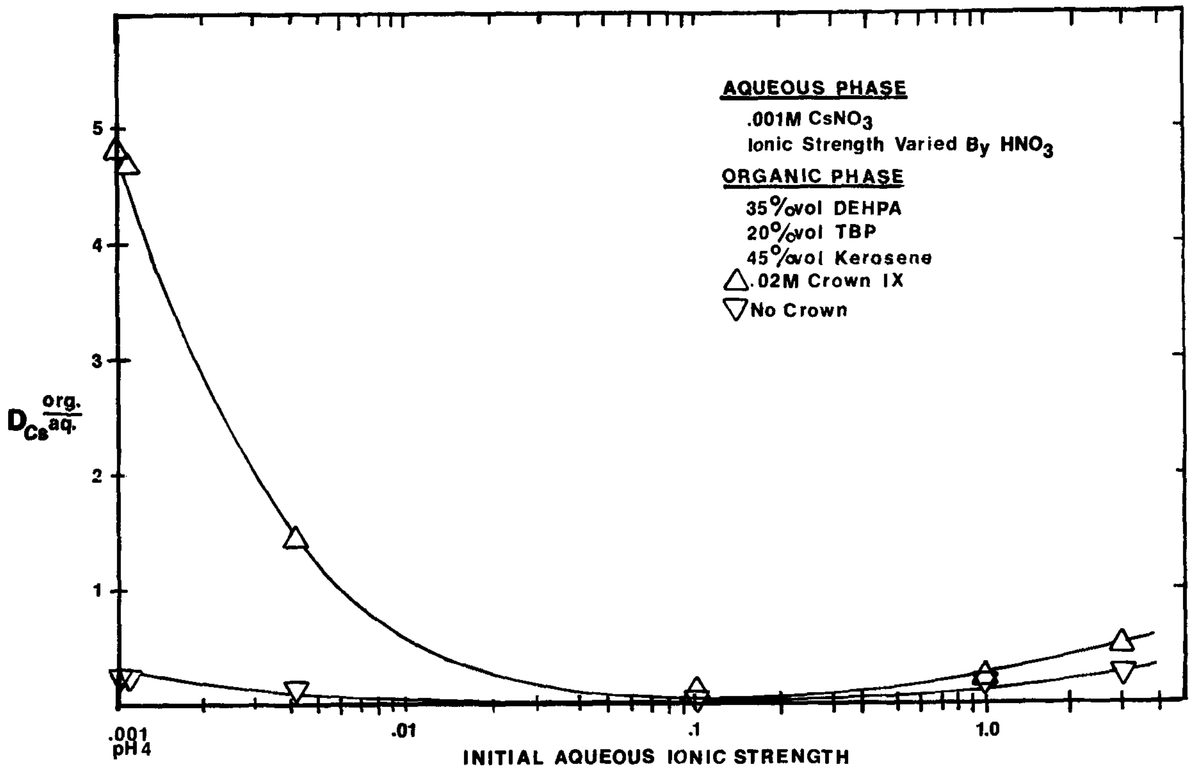

FIG. 10. Cesium distribution with Crown IX in 35% DEHPA–20% TBP–kerosene.

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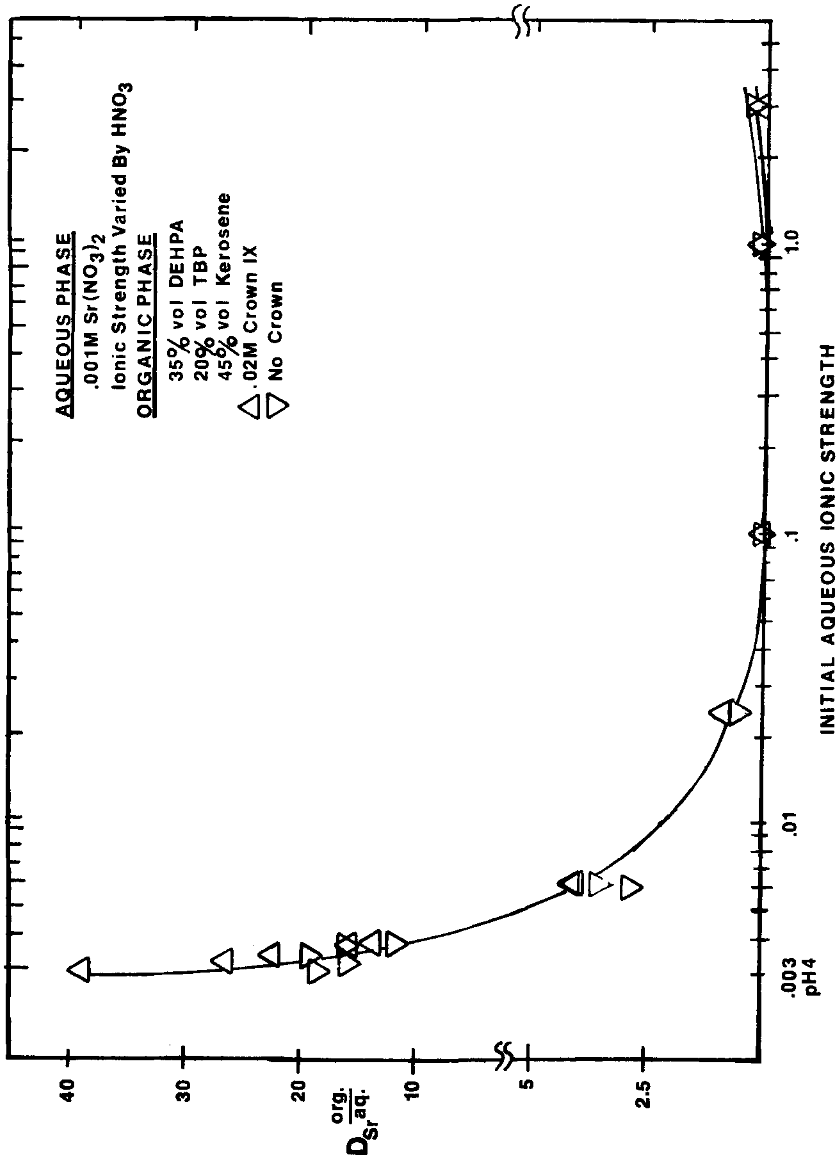

FIG. 11. Strontium distribution with Crown IX in 35% DEHPA–20% TBP–kerosene.

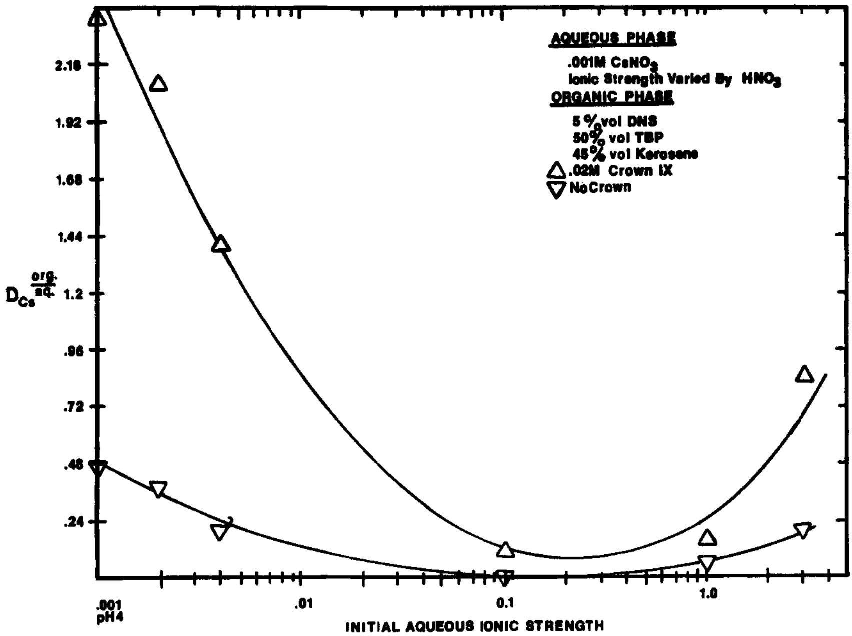

FIG. 12. Cesium distribution with Crown IX in 5% DNS–50% TBP–kerosene.

centration of 1.5 *M*. The drop to zero as the acid concentration increases to 3 *M* is attributed to protonation of the crown.

Organic Anions

Due to the lack of success with the inorganic anions, two organic acids were tested as organic anion suppliers to determine their effect on extraction. They were didodecylnaphthalene sulfonic acid (DNS) and di-2-ethylhexyl phosphoric acid (DEHPA).

The addition of these organic anion suppliers dramatically improved the extraction of the metals. In Fig. 7, distribution data for both Cs^+ and Sr^{2+} using DNS in combination with 12 different crowns are shown. All the distribution coefficients for Sr^{2+} are within a range of 4 to 5.5 for these test conditions. Most of the distribution coefficients for Cs^+ are within a range of 0 to 0.5 except for the distribution coefficient with Crown IX. This crown extracted the Cs^+ appreciably better than any of the other crowns tested. For this reason all further distribution coefficients were determined using Crown IX and DNS or DEHPA while varying the other parameters in both the aqueous and organic phases.

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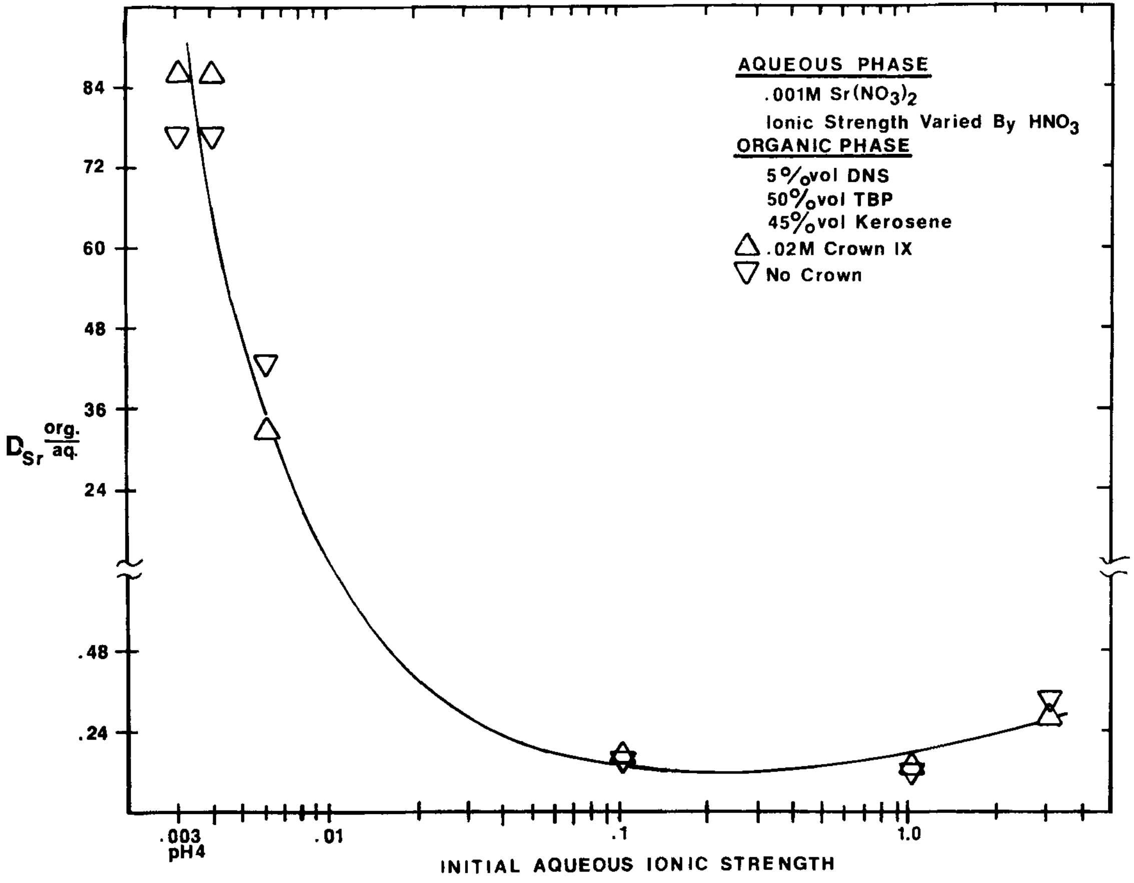

FIG. 13. Strontium distribution with Crown IX in 5% DNS–50% TBP–kerosene.

Analysis of Extraction Data in Terms of the Two Extraction Models

All the definitive distribution data for both Cs^+ and Sr^{2+} are shown in Figs. 8 through 13 (see also Figs. 14–16). Previously two major extraction models were discussed: (a) metal extraction with crown and organic anion supplier, and (b) extraction with organic anion suppliers only.

The value for n is 1 for Cs^+ and 2 for Sr^{2+}. The values of K_{eq} and $K_{eq'}$ are expected to be higher for Cs^+ than for Sr^{2+}, as discussed previously.

The Cs^+ distribution data shown in Figs. 8, 10, and 12 clearly show that with either DNS or DEHPA supplying the organic anion, useful extraction requires a complex containing both the crown and DNS or DEHPA. The best results were obtained from an aqueous phase initially 3 M HNO_3 into an organic phase of 5 vol-% DNS–27 vol-% TBP–68 vol-% kerosene, which is of interest for compatibility with the Purex process (Fig. 8). Changing the solvent to 50 vol-% TBP–45 vol-% kerosene (Fig. 12) lowered the $D_{org/aq}$ over the whole range of ionic strength. The increase in TBP concentration increased both the water and HNO_3

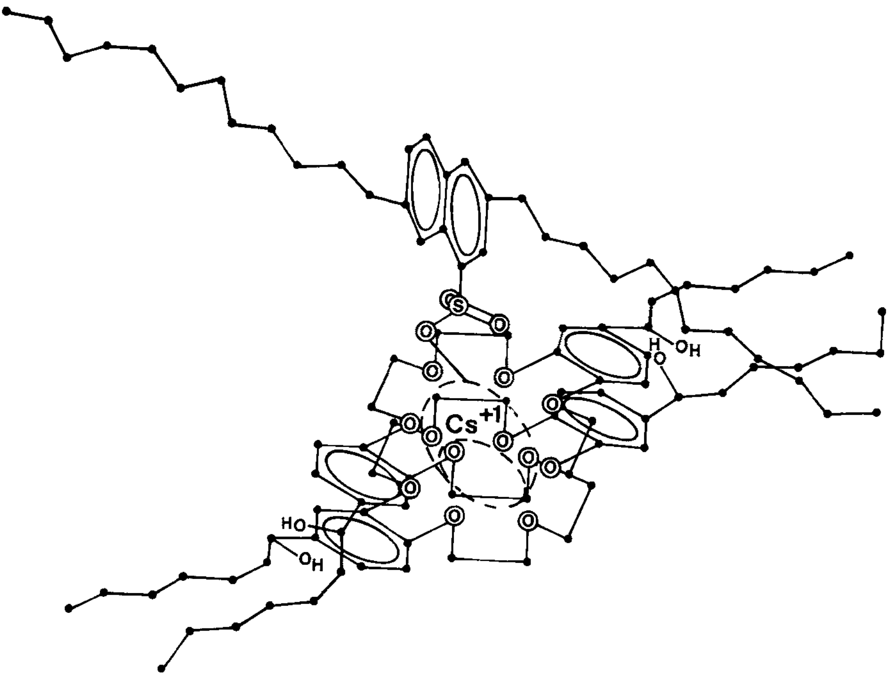

FIG. 14. Isometric representation of a Cs^+ atom complexed by two Crown IX's and one DNS molecule.

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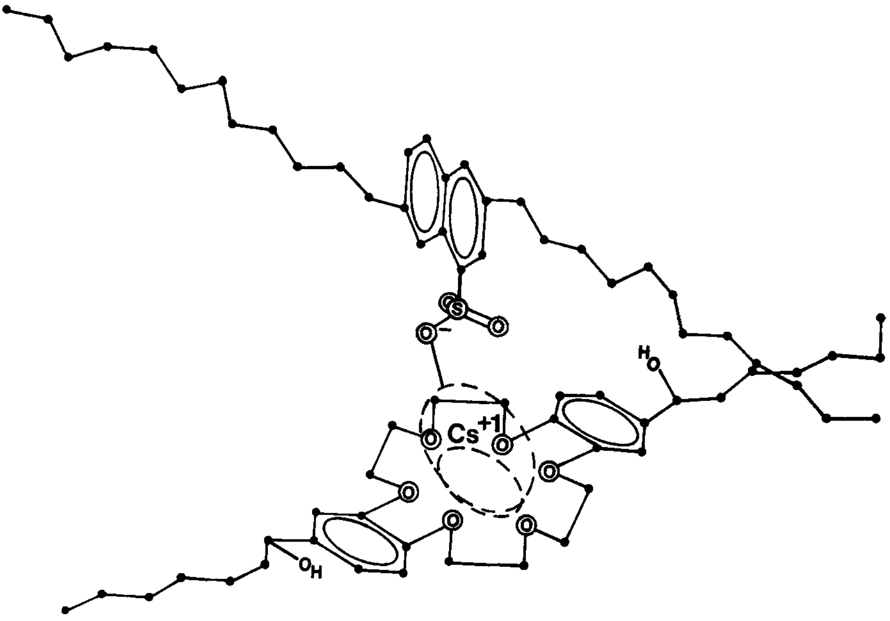

FIG. 15. Isometric representation of a Cs^+ atom complexed by one Crown IX and one DNS molecule.

content of the organic phase, particularly in the high acid region. This increase of HNO_3 and H_2O concentration will have at least two effects:

(1) By increasing the aqueous character, the complex's solubility may be decreased due to its strongly hydrophobic nature.
(2) H_2O and HNO_3 may hydrogen bond with the crown oxygens, reducing the crowns' availability for complexing.

When DEHPA was used in place of DNS as the organic anion (35 vol-% DEHPA–20 vol-% TBP–45 vol-% kerosene, Fig. 10), the results were very similar to those with 50 vol-% TBP and DNS (Fig. 12).

The upturn in the Cs^+ distribution coefficient in 3 *M* HNO_3 is not predicted by the proposed models but may well be due to the large increase in HNO_3 and water in the organic phase as the aqueous phase acidity is increased.

The Sr^{2+} distribution data shown in Figs. 9, 11, and 13 show no difinitive difference with or without the presence of the crown, indicating that liquid ion exchange controls the extraction. Since Crown IX is an 18-crown-6 whose cavity should fit Sr^{2+} better than Cs^+ (Table 1), it is

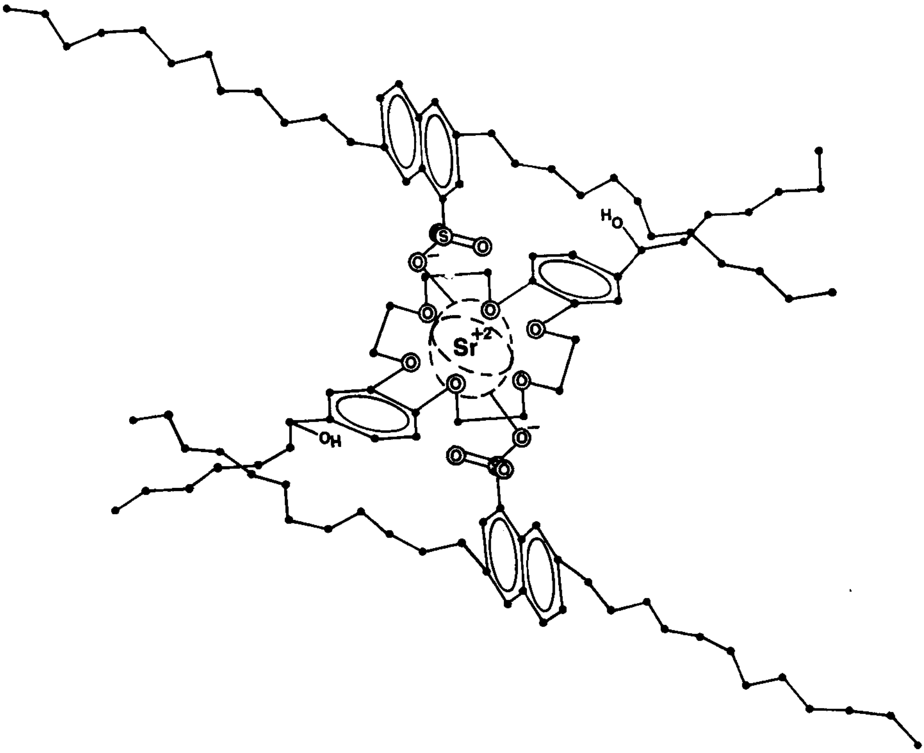

FIG. 16. Isometric representation of a Sr^{2+} atom complexed by one Crown IX and two DNS molecules.

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hypothesized that the long side chains of both the DNS or DEHPA and the crown cause sufficient steric hindrance to prevent the formation of the crown complex. In the 3 *M* HNO_3 region the Sr^{2+} extracts very poorly and should be easy to separate from the Cs^+. The distribution coefficients in the low acid region are much higher for Sr^{2+} than Cs^+, which is predicted by the models.

Conclusions

(1) The system of the bis-(4,4′(5′)-[1-hydroxyheptyl]-benzo)-18-crown-6 (IX) in 5% DNS–27% TBP in kerosene can be used to separate Cs^+ from Sr^{2+} and La^{3+}. It is the first solvent extraction process developed capable of this separation. This system can be used in conjunction with the Purex process currently used at the Savannah River Plant. Steric effects due to large anion size prevent

La^{3+} from extracting at pH's up to 4, while in the low acid region Sr^{2+} extracts by a liquid ion-exchange mechanism and the addition of crown does not significantly improve the distribution.

(2) The effect of the anion in two-phase solvent extraction is much more important than had previously been supposed.

(3) The use of branched side chains on the benzene rings in the dibenzo crowns gives much greater organic solubility than the straight chains.

(4) As might be expected, increasing the side chain length increases solubility up to a chain length of about seven and then decreases its solubility as the chain lengths are made longer.

(5) Hydrogenating the benzene rings attached to the crown to cyclohexyl increases the crown solubility in both organic and aqueous phases.

(6) Steric effects cause Crown IX to give much better organic to aqueous distribution because of the hydrophobic nature given to the Cs^+ by the seven carbon straight chains attached to the benzene rings on dibenzo-18-crown-6.

(7) The size of the crown cavity as compared to the size of the metal ion seems much less important than previously believed, at least in two-phase (aqueous–organic) solvent extraction.

(8) Radiation stability tests of Crown IX in 5% DNS–27% TBP–68% kerosene at 10^7 rd, which is far in excess of the exposure expected in a centrifugal mixer settler, gave about a 12–14% reduction in the distribution coefficient for Cs^+ org/aq when irradiated in contact with 10^{-4} M HNO_3. The same solution when irradiated in contact with 3 M HNO_3 showed a much larger drop in the distribution coefficient. Radiation stability of the crowns will be discussed in much greater detail in a subsequent paper.

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