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Effect of Macrocycle Type on the Extraction into Toluene of Ag^+, Pb^{2+}, and Cd^{2+} Using a Combination of a Macrocycle and Di(2-ethylhexyl)phosphoric Acid as Extractants

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Abstract

The nitrate salts of Ag^+ and Pb^{2+} are extracted into toluene solutions of one of the following macrocycles: dicyclohexano-18-crown-6 (DC18C6); 1,10-dithia-18-crown-6 (DT18C6); 1,10-diaza-18-crown-6 (2.2); hexathia-18-crown-6 (HT18C6); or cryptand 2.2.1. In addition, the nitrate salt of Cd^{2+} is extracted into toluene solutions of DC18C6 or DT18C6. Ag^+, Pb^{2+}, and Cd^{2+} are also extracted into toluene containing di(2-ethylhexyl)phosphoric acid (HDEHP) and toluene containing a combination of HDEHP and one of the macrocycles. Metal ion extraction is synergistic for the systems containing HDEHP and DC18C6, 2.2, or 2.2.1, but is antagonistic for the systems containing HDEHP and DT18C6 or HT18C6.

INTRODUCTION

Neutral (*1, 2*) and ionizable (*3, 4*) macrocycles have been used to extract cations into organic solvents. When neutral macrocycles are used as extractants, very little salt extraction occurs for salts containing hard anions such as NO_3^- or Cl^-. For this reason, acidic extractants have been used in conjunction with neutral macrocycles in an effort to increase cation extraction from salt solutions containing hard anions (*5–7*). The presence of acidic extractants in the organic phase increases cation

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extraction because of the exchange of protons for cations. We reported a study of metal ion extraction into toluene using DC18C6 and/or HDEHP as extractants (*7*). The significant findings of this earlier work were: 1) metal ion extraction was small using only DC18C6 as extractant, and 2) metal ion extraction was synergistic when a combination of DC18C6 and HDEHP was used. A desire to know the effects on metal ion extraction using different macorcycle types led to the present study. The objective of this study has been to investigate the effect of macrocycle type upon Ag^+, Pb^{2+}, and Cd^{2+} extraction into toluene with and without HDEHP present in the organic phase. The selection of macrocycles was based primarily upon donor atom type. The macrocycles studied are shown in Fig. 1.

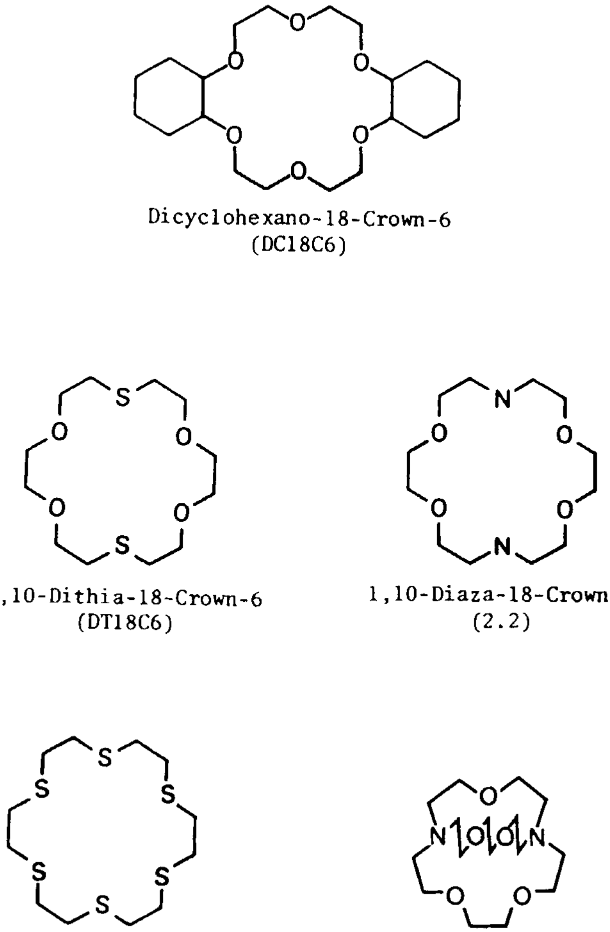
EXPERIMENTAL

Procedures

An aqueous solution (3.0 mL) containing 1.0×10^{-4} M $M(NO_3)_n$ was added to a 10-mL Erlenmeyer flask containing 3.0 mL of toluene which was 0.125 M in HDEHP and/or 0.100 M in macrocycle and/or 0.001 M in macrocycle. The two phases were shaken mechanically by wrist action in a constant temperature water bath at 25.0°C. After a period of 20 min the shaker was stopped and the phases allowed to separate. A portion of the aqueous phase was removed and analyzed for the appropriate metal using a Perkin-Elmer Model 603 atomic absorption spectrophotometer. Determination of aqueous phase metal concentrations before and after equilibration with toluene allowed for the calculation of metal ion distribution ratios, $D_{M^{n+}}$. The calculated $D_{M^{n+}}$ values were based on four separate determinations that were made for each metal and reagent combination. A Q test was used as a basis for discarding outlying data points (*8*).

Reagents

The following chemicals were obtained from the indicated suppliers and were used without further purification: toluene (Fisher reagent), $AgNO_3$ and $Pb(NO_3)_2$ (Aldrich gold label), $Cd(NO_3)_2$ (B&A reagent), HDEHP (Mobil), DC18C6 and DT18C6 (Parish), 2.2 and 2.2.1 (MCB), and HT18C6 (Professor Stephen Cooper, Harvard University). In the case of DC18C6, the isomers were not separated.



Dicyclohexano-18-Crown-6
(DC18C6)

1,10-Dithia-18-Crown-6
(DT18C6)

1,10-Diaza-18-Crown-6
(2.2)

Hexathia-18-Crown-6
(HT18C6)

Cryptand 2.2.1

FIG. 1. Macrocycles.

RESULTS AND DISCUSSION

Tables 1 and 2 contain metal ion distribution ratios, $D_{M^{n+}} = [M]_{\text{toluene}}/[M^{n+}]_{\text{water}}$, for the nitrate salts of Ag^+, Pb^{2+}, and Cd^{2+}. The data in Table 1 are for toluene solutions 0.100 *M* in macrocycle and the data in Table 2 are for toluene solutions 0.001 *M* in macrocycle. The low macrocycle concentrations in Table 2 are a result of the limited quantities of the macrocycles HT18C6 and 2.2.1 that were available for use.

Log *K* values for M^{n+}-macrocycle interaction may be used to approximate the ability of macrocycles to extract metal ions. Generally, M^{n+} extraction, and therefore $D_{M^{n+}}$, would be expected to increase with increasing log *K* values for M^{n+}-macrocycle interaction. In Table 1, D_{Ag^+} increases with increasing log $K(H_2O)$ values for Ag^+-macrocycle interaction, except for the Ag^+–2.2 system. In the case of Pb^{2+}, $D_{Pb^{2+}}$ increases with increasing log $K(H_2O)$ values for Pb^{2+}-macrocycle interaction, except for the Pb^{2+}–DC18C6 system. In Table 2, $D_{M^{n+}}$ is greater for the macrocycle that gives the larger log $K(H_2O)$ value for both Ag^+-macrocycle and Pb^{2+}-macrocycle interaction. In the Ag^+–2.2 and Pb^{2+}–DC18C6 systems of Table 1, other factors, such as macrocycle distribution and *M*-macrocycle^{n+} distribution between the organic and aqueous phases, may be more important parameters than log *K* values for predicting $D_{M^{n+}}$. The $D_{M^{n+}}$ data in Tables 1 and 2 also show that for a given macrocycle the metal ion with the largest log $K(H_2O)$ value for M^{n+}-macrocycle interaction is extracted to the greatest degree except for the cases of DC18C6 and 2.2. Again, other parameters may have to be considered in the cases of these two macrocycles.

TABLE 1

Distribution Coefficients, $D_{M^{n+}}$, between Toluene and Water for the Nitrate Salts of Ag^+, Pb^{2+}, and Cd^{2+} and log $K(H_2O)$ Values for M^{n+}-Macrocycle Interaction[a]

	Macrocycle					
	DC18C6		DT18C6		2.2	
Metal ion	$D_{M^{n+}}$	Log *K*	$D_{M^{n+}}$	Log *K*	$D_{M^{n+}}$	Log *K*
Ag^+	0.10[b]	2.1[c]	0.15 ± 0	4.34[c]	0	7.90[c]
Pb^{2+}	0[b]	4.8[c]	0.06 ± 0.06	3.13[c]	0.09 ± 0.05	6.90[c]
Cd^{2+}	0.03 ± 0.02		0.09 ± 0.03			

[a] $[M^{n+}]_{aq} = 1.0 \times 10^{-4}$ and $[DC18C6]_{org} = [DT18C6]_{org} = [2.2]_{org} = 0.100$ before extraction. Each $D_{M^{n+}}$ is the average of four determinations.

[b] From Ref. 7.

[c] From Ref. 9.

TABLE 2
Distribution Coefficients, $D_{M^{n+}}$, between Toluene and Water for the Nitrate Salts of Ag^+ and Pb^{2+} and Log $K(H_2O)$ Values for M^{n+}-Macrocycle Interaction[a]

	Macrocycle			
	HT18C6		2.2.1	
Metal ion	$D_{M^{n+}}$	Log K	$D_{M^{n+}}$	Log K
Ag^+	0.08 ± 0.02	12[b]	0.02 ± 0.03	10.16[c]
Pb^{2+}	0.03 ± 0.02	1[b]	0.20 ± 0.04	13.13[c]

[a] $[M^{n+}]_{aq} = 1.0 \times 10^{-4}$, $[HT18C6]_{org} = [2.2.1]_{org} = 0.001$ before extraction. Each $D_{M^{n+}}$ is the average of four determinations.

[b] Log $K(H_2O)$ values are estimated.

[c] From Ref. 9.

In Tables 3 and 4, $D_{M^{n+}}$ values are given for metal ion extractions with toluene solutions containing a macrocycle and/or HDEHP. When $D_{M^{n+}}$ for the two reagents used together is greater than the sum of the $D_{M^{n+}}$ values for the two reagents used separately, the extraction is said to be synergistic. In the previous study we showed that DC18C6 and HDEHP extracted K^+, Tl^+, Ag^+, and Pb^{2+} synergistically (*7*). The reasons for this effect were discussed in terms of ion solvation, i.e., solvation of M-DC18C6^{n+} is much lower than that of M^{n+}. Thus, formation of a M-DC18C6^{n+} complex enhances partitioning of inorganic salts from aqueous solutions into organic solvents. This enhancement is further aided by the lipophilic exterior of the M-DC18C6^{n+} complex. The M-DC18C6^{n+} complex is extracted with an anion to the organic phase in order to maintain electroneutrality. Although salt extraction into organic phases increases because of M-DC18C6^{n+} complex formation, poor salt extraction still occurs for salts containing anions with large hydration energies. The presence of HDEHP provides, under the right pH conditions, the lipophilic anion, $DEHP^-$, which enhances the extraction of the M-DC18C6^{n+} complex into the organic phase. Kinard et al. (*5*) found that among alkali cations, synergistic effects using HDEHP and DC18C6 were greatest for K^+ and Rb^+, whose ionic radii most closely matched the cavity radius of DC18C6.

In the present study, Cd^{2+} was also extracted synergistically with DC18C6 and HDEHP while Ag^+ and Pb^{2+} were extracted synergistically with either 2.2 or 2.2.1 and HDEHP. In the cases of the nitrogen-containing macrocycles, 2.2 and 2.2.1, the synergistic effect may be a result primarily of HDEHP deprotonation and the formation of an excess of $DEHP^-$ to interact with the M-macrocycle^{n+} complex. It is

TABLE 3

Values of $D_{M^{n+}}$ for Extraction of M^{n+} by a Macrocycle and HDEHP, Used Separately and Together[a]

Extractant	Ag^+	Pb^{2+}	Cd^{2+}
HDEHP	0.19[b]	9.17[b]	0.13 ± 0.03
DC18C6	0.10[b]	0[b]	0.03 ± 0.02
HDEHP + DC18C6	1.03[b]	46.9[b]	0.23 ± 0.02
DT18C6	0.15 ± 0	0.06 ± 0.06	0.09 ± 0.03
HDEHP + DT18C6	0	1.15 ± 0.15	0.12 ± 0.02
2.2	0	0.09 ± 0.05	
HDEHP + 2.2	>1.84 ± 0.18[c]	>45.31 ± 15.16[c]	

[a] $[M^{n+}]_{aq} = 1.0 \times 10^{-4}$, $[HDEHP]_{org} = 0.125$, $[DC18C6]_{org} = [DT18C6]_{org} = [2.2]_{org} = 0.100$ before extraction. Each $D_{M^{n+}}$ is the average of 4 determinations.

[b] From Ref. 7.

[c] A white emulsion formed in the aqueous phase upon equilibration with the organic phase.

known that 2.2 and 2.2.1 are strong bases (*9*) and that they hydrolyze water to form basic solutions. In the previous study we found K^+ extraction to increase exponentially with increasing aqueous phase pH when both DC18C6 and HDEHP were present in the toluene phase (*7*). In order to understand the effects of pH upon metal ion extraction in the present study, a 3.0-mL toluene solution containing HDEHP or HDEHP and one of four macrocycles was equilibrated for 20 min with 3.0 mL of distilled deionized water. After phase separation, a portion of the aqueous phase was removed and the pH measured. The measured aqueous phase pH and the initial toluene solution (in parentheses) were: 2.65 (0.125 *M* HDEHP); 2.90 (0.100 *M* DC18C6 and 0.125 *M* HDEHP); 2.65 (0.100 *M* DT18C6 and 0.125 *M* HDEHP); 2.70 (0.001 *M* HT18C6 and 0.125 *M* HDEHP); 3.03 (0.001 *M* 2.2.1 and 0.125 *M* HDEHP). These results show that an increase in aqueous phase pH does not always result in greater extraction, since DC18C6 produces greater synergistic extraction than 2.2.1 even though the pH of the aqueous phase in the case of DC18C6 is lower than in the case of 2.2.1.

The sulfur-containing macrocycles, DT18C6 and HT18C6, produce antagonistic extractions of Ag^+ and Pb^{2+}. The reasons for this effect are not clearly understood. The effect may be a result of macrocycle coordination to M^{n+} in such a manner as to prevent optimal interaction of the M-macrocycle^{n+} complex by $DEHP^-$. Complex formation between

TABLE 4
Values of $D_{M^{n+}}$ for Extraction of M^{n+} by a Macrocycle and HDEHP, Used Separately and Together[a]

Extractant	Ag^+	Pb^{2+}
HDEHP	0.19[b]	9.17[b]
HT18C6	0.08 ± 0.02	0.03 ± 0.02
HDEHP + HT18C6	0.24 ± 0.02	2.83 ± 0.09
2.2.1	0.02 ± 0.03	0.20 ± 0.04
HDEHP + 2.2.1	0.51 ± 0.10	9.92 ± 1.33

[a] $[M^{n+}]_{aq} = 1.0 \times 10^{-4}$, $[HDEHP]_{org} = 0.125$, $[HT18C6]_{org} = [2.2.1]_{org} = 0.001$ before extraction. Each $D_{M^{n+}}$ is the average of 4 determinations.
[b] From Ref. 7.

HDEHP and the sulfur-substituted macrocycles may also be a cause of the antagonistic extraction. The existence of such complexes would be expected to decrease the availability of HDEHP and the macrocycles for interactions with metal ions.

CONCLUSIONS

The significant results of this study are that synergistic cation extraction occurs with HDEHP and a combination of one of the following macrocycles: DC18C6, 2.2, or 2.2.1. This synergistic effect is particularly high in the case of the Ag^+–2.2 system, where the combination of reagents increases D_{Ag^+} ninefold over the sum of D_{Ag^+} for the two reagents used separately. Further extraction studies need to be conducted in order to determine the effect of combining reagents upon selectivity factors for the extraction of metal ions from metal ion mixtures.

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