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Solvent Extraction of the Nitrate Salts of K^+, Ag^+, Tl^+, and Pb^{2+} Using Di(2-Ethylhexyl) phosphoric Acid and Dicyclohexano-18-Crown-6 in Toluene

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ABSTRACT

A solvent extraction system is used to determine metal distribution coefficient, $D_{M^{n+}}$, values between water and toluene for the nitrate salts of K^+, Ag^+, Tl^+, and Pb^{2+} using, both individually and together, the organic soluble complexing agents HDEHP and DC18C6 (Figure 1). Synergistic solvent extraction effects are found for all of the metals examined. The extraction of Pb^{2+} is much greater than that of the monovalent cations. The extraction of K^+ increases either as the equilibration temperature decreases or as the equilibrated aqueous pH increases. The extraction of Ag^+ increases in a regular fashion until the initial concentration of DC18C6 in the toluene reaches the initial concentration of HDEHP in the toluene. Beyond this point, no appreciable increase in Ag^+ extraction is observed with increased initial DC18C6 concentration.

INTRODUCTION

Macrocycles such as dicyclohexano-18-crown-6, DC18C6, (Figure 1) are capable of selectively complexing cations in cases where the size of the cation matches that of the macrocycle cavity (2,3). In addition to an electron rich interior, macrocycles

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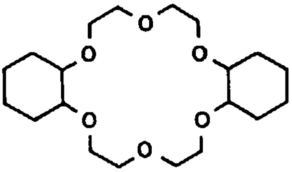
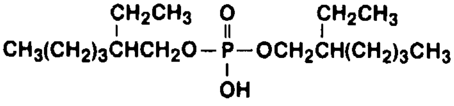
possess a hydrophobic exterior which facilitates the solubilization of ionic salts in organic solvents. This property of macrocycles has led to extensive studies on their use in the solvent extraction of metal salts into organic phases. Pedersen extracted alkali metal picrates from water into toluene with a series of crown ethers (4). He found K-picrate to be extracted more than the other alkali metal picrates using DC18C6. Similarly, Na-picrate was found to be extracted more than any other alkali metal picrate using *m*-*tert*-butylcyclohexano-15-crown-5. These results indicate that the extraction of the metal-macrocycle complex is related to the fit of the cation in the crown ether cavity. Among the alkali metals, the ionic radius of K^+ matches best that of the DC18C6 cavity (3). Likewise, Na^+ fits the *m*-*tert*-butyl cyclohexano-15C5 cavity better than the other alkali metal ions which likely accounts for its better extraction. Others have extracted metal picrates into organic solvents using macrocycles of the crown ether and cryptand types (5-7). Recently, Kinard, McDowell, and Shoun have used crown ethers in conjunction with di(2-ethylhexyl)phosphoric acid, HDEHP, (Figure 1), in the solvent extraction of alkali and alkaline earth metal ions (8). In these systems, the combined or synergistic effect of these reagents was to increase the D_M^{n+} values, over the sum of the D_M^{n+} values for the two reagents used separately. D_M^{n+} is defined by equation (1) as



Dicyclohexano-18-crown-6 (DC18C6)



$$\mathrm{CH_3(CH_2)_3\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}HCH_2O-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-OCH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}H(CH_2)_3CH_3}$$

Di(2-ethylhexyl) phosphoric acid (HDEHP)

FIGURE 1. Extraction reagents used in the study.

the ratio of the metal-containing species in the organic and aqueous phases, respectively.

$$D_{M^{n+}} = \frac{[M]_{org}}{[M]_{aq}} \qquad (1)$$

Besides the use of macrocycles in solvent extraction, previous studies have described liquid membrane systems for the transport of metal salts across a chloroform membrane using various macrocyclic carriers (9-14). A significant finding in these studies was that increase in the stability of the metal-macrocycle complex resulted in increased metal transport until complex stability became too large for effective decomplexation of metal ions at the receiving phase boundary.

In this paper, we report a synergistic effect in the solvent extraction of the nitrate salts of K^+, Ag^+, Tl^+, and Pb^{2+} using HDEHP and DC18C6. Values of $D_{M^{n+}}$ were determined using HDEHP and DC18C6 individually and together. The extraction of K^+ was also determined as a function of temperature and pH and the Ag^+ extraction was measured as a function of the initial concentration of DC18C6 at constant initial HDEHP concentration in the toluene.

EXPERIMENTAL

Experiments were performed by equilibrating 5 ml of distilled deionized water which contained 10^{-4} F $M(NO_3)_n$ with 5 mL of toluene which contained 0.100 F DC18C6 and/or 0.125 F HDEHP in 25 mL Erlenmeyer flasks. The flasks were mechanically agitated by a wrist action shaker for 15 minutes while immersed in a constant temperature water bath. Preliminary experiments showed that the two phases equilibrated in less than 5 minutes. Upon equilibration, the two phases were allowed to separate and a portion of the aqueous phase was removed and analyzed for the appropriate metal by atomic absorption spectrophotometry. The concentration of the metal in the aqueous phase before extraction was obtained in the same manner. In addition, the pH of the equilibrated aqueous phase was measured with a glass-reference combination electrode. The extraction of K^+ was studied as a function of temperature and pH. In these cases the pH of the KNO_3 solutions was adjusted by adding 50% KOH to the aqueous KNO_3 solution before extraction. The calculated $D_{M^{n+}}$ values were based on eight separate determinations which were made for each metal and reagent combination and, in the case of D_{K^+}, for each temperature and pH value. A Q test was used as a basis for discarding outlying data points (15).

The chemicals used together with their suppliers are: KNO_3 and toluene (reagent grade-Fisher); $AgNO_3$, $TlNO_3$, and $Pb(NO_3)_2$ (gold label-Aldrich); HDEHP (Sigma and Mobil); and DC18C6 (Parish). The chemicals were used without further purification and, in the case of DC18C6, the isomers were not separated.

RESULTS AND DISCUSSION

Values of $D_{M^{n+}}$ for $M^{n+} = K^+$, Ag^+, Tl^+, and Pb^{2+} are tabulated in Table 1 for the extracting reagents HDEHP and DC18C6 used separately and together. In each case, the concentration of the metal in the organic phase is calculated from the difference between the concentrations of the metal in the aqueous phase before and after extraction. The extraction results in Table 1

TABLE 1
Values of $D_{M^{n+}}$ for Extraction of Several M^{n+} by DC18C6 and HDEHP, used Separately and Together.[a] T = 25.0°C.

	KNO_3	$AgNO_3$	$TlNO_3$	$Pb(NO_3)_2$
DC18C6	0	0.10	0	0
HDEHP	0(2.57)	0.19(2.67)	0(2.68)	9.17(2.62)
DC18C6 + HDEHP	0.21(2.74)	1.03(2.88)	1.13(2.99)	46.9(2.83)

[a] $[M(NO_3)_n] = 10^{-4}$ F, $[HDEHP]_{org} = 0.125$ F, and $[DC18C6]_{org} = 0.100$ F before extraction. Each $D_{M^{n+}}$ value is the average of either seven or eight determinations. The standard deviation in each case is ±30% or less. Each pH value (reported in parentheses) is the average of four separate determinations.

can be understood by considering the expected solvation of the several cations and anions involved in the extraction process and the relative stabilities of the complexes formed by M^{n+} with the extracting reagents.

Partition coefficients for alkali metal nitrates between water and organic solvents are generally very small. For example, the D_{RbNO_3} value between water and chloroform is 1.03 x 10^{-5} (16). Similar values would be expected in the metal-water-toluene systems studied here. The small values for partitioning of metal nitrates into organic solvents may be attributed to the appreciable hydration energies of M^{n+} and NO_3^-. One would expect improvement in metal partitioning from water to toluene when either, in the aqueous phase, M^{n+} is replaced by a large hydrophobic cation such as $MDC18C6^{n+}$ or, in the organic phase, a hydrophobic acid such as HDEHP is present whose anion is capable of forming a complex with M^{n+}. The combination of these two effects should result in even more effective extraction of M^{n+} since the energy expenditure required to remove M^{n+} from the aqueous phase is markedly reduced. The results in Table 1 are consistent with these expectations. When the two extraction reagents are used separately, improved extraction is seen for Ag^+ and Pb^{2+} in the case of HDEHP and for Ag^+ in the case of DC18C6. In the remaining cases, involving either HDEHP or DC18C6 alone, any improvement is apparently too small to be measured using our technique. When HDEHP and DC18C6 are used together, M^{n+} extraction in all cases is much greater than when either reagent is used alone, with Pb^{2+} showing the greatest increase. The greater extraction of Pb^{2+} over the M^{n+} species using both HDEHP and DC18C6 is probably a result of two effects. First, even though the extraction data do not give an indication as to the location of complex formation, the log $K(H_2O)$ data in Table 2 suggest that a greater percentage of the crown complex will be formed in the case of Pb^{2+}. These log K data show that all four metal ions form stable complexes in aqueous solution with DC18C6, but the stability of the complex formed by Pb^{2+} is more than 100 times larger. Second, electroneu-

TABLE 2

Log Values[a] of $K=[MDC18C6^{n+}]/[M^{n+}][DC18C6]$ for the Aqueous-Phase Reaction M^{n+} + DC18C6 = $MDC18C6^{n+}$

DC18C6	K^+	Ag^+	Tl^+	Pb^{2+}
cis-syn-cis Isomer	2.02 1.91(40°C)[b]	2.36	2.44	4.95
cis-anti-cis Isomer	1.63 1.50(40°C)[b]	1.59	1.83	4.43

[a]Values are taken from reference 17 and are valid in H_2O at 25°C except as indicated. [b]Values are taken from reference 18, and are valid in H_2O.

trality requires that two $DEHP^-$ ions interact with the $Pb\text{-}DC18C6^{2+}$ complex while only one $DEHP^-$ ion interacts with the $M\text{-}DC18C6^+$ complexes. Since the M^{n+} lies in the DC18C6 cavity, solvation of the M^{n+} in the complex occurs primarily at the two axial positions. Thus, the Pb^{2+} is more completely desolvated by the combined effect of DC18C6 and two $DEHP^-$ ions than is M^+ where only one $DEHP^-$ ion is present. Further insight into the extraction process would be provided by log K data for the interaction of $DEHP^-$ with the M^{n+} and $M\text{-}DC18C6^{n+}$ species studied. However, these data are not available.

The extraction of K^+ into toluene by the combined use of DC18C6 and HDEHP is seen in Figure 2 to decrease as the temperature increases indicating an exothermic extraction reaction. This decreased partitioning is consistent with the known increase in aqueous solubilities of KNO_3 and KOH as the temperature is raised (19), with the increased pK value of HDEHP in aqueous solution at 40°C (pK = 2.00) compared to that at 25°C (pK = 1.72) (20), and with the decreased log K value for K^+-DC18C6 interaction from 25 to 40°C (Table 2). However, log K values for the reaction of K^+ with $DEHP^-$ as a function of temperature need to be considered as

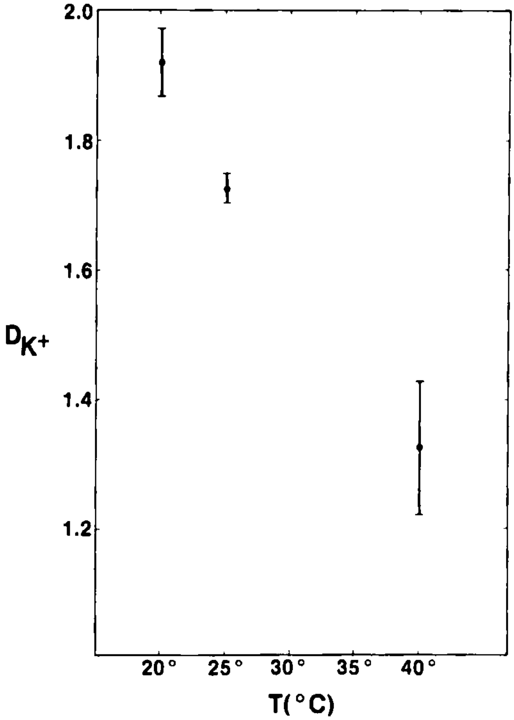


FIGURE 2. Effect of temperature on extraction of K^+ by DC18C6 + HDEHP. The concentration of K^+ following addition of KOH and immediately prior to extraction is 7.1 x 10^{-3} M.

well in arriving at an explanation of the extraction results. Unfortunately, these data are unavailable.

In Figure 3, the D_{K^+} value in the presence of HDEHP and DC18C6 is seen to increase in exponential-like fashion as the pH of the aqueous phase is raised. The increase in D_{K^+} as pH increases indicates that OH^- is reacting with HDEHP, freeing $DEHP^-$ which, in turn, interacts with the cation to form a neutral, extractable species.

The effect on D_{Ag^+} of varying the initial DC18C6 concentration as the concentration of HDEHP is held constant is given in

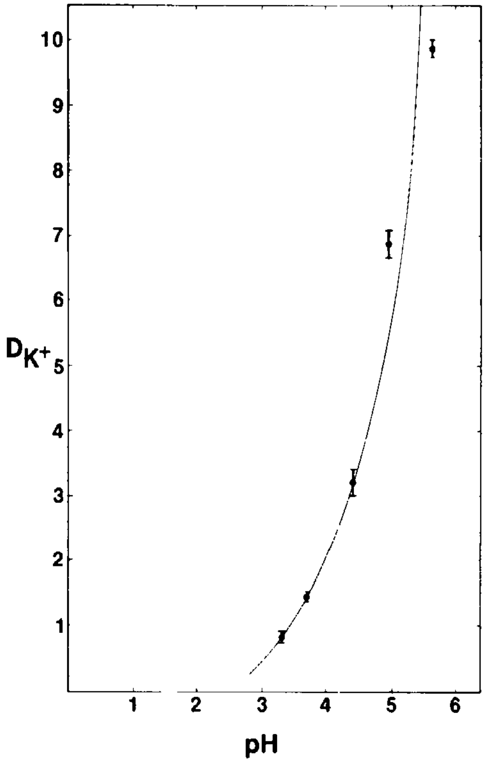


FIGURE 3. Effect of pH on extraction of K^+ by DC18C6 + HDEHP at 23.5 ± 0.3°C. The K^+ concentration of the several solutions following addition of KOH and immediately prior to extraction varies from 1.8×10^{-3} M to 3.5×10^{-2} M, with the highest K^+ concentration corresponding to the solution of highest pH.

TABLE 3

Values of D_{Ag^+} as a Function of the Formal Concentration of DC18C6 at Constant HDEHP Concentration (0.125F).[a] T = 25.0°C

$[DC18C6]_{org}$	0	0.010	0.030	0.050	0.100	0.200
D_{Ag^+}	0.19	0.23	0.30	0.48	1.03	1.05

[a] The concentration of the $AgNO_3$ in the aqueous phase is 10^{-4} F. $[DC18C6]_{org}$ refers to the formal concentration of DC18C6 in the toluene phase before equilibration with the $AgNO_3$ solution. The D_{DC18C6} between chloroform and water is 454 (14). A similar D_{DC18C6} value would be expected for the toluene-water system. Therefore, little loss of DC18C6 to the aqueous phase is expected. Each D_{Ag^+} value is the average of either seven or eight determinations. The standard deviation in each case is ±30% or less.

Table 3. The D_{Ag^+} value increases significantly with increased initial DC18C6 concentration until a DC18C6 concentration equal to that of the HDEHP is reached. Beyond this point, continued increase in the concentration of DC18C6 does not result in increased D_{Ag^+}. This result is consistent with the formation of a $M\text{-}DC18C6^+$ complex in which the positive charge is diffused over a greater volume than is the case with the hydrated cation. This $M\text{-}DC18C6^+$ cation is then extracted with much less energy expenditure by the $DEHP^-$ ion.

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