THERMODYNAMICS OF THE EXTRACTION OF SELECTED METAL IONS BY DI(2-ETHYLHEXYL) ALKYLENEDIPHOSPHONIC ACIDS

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The thermodynamics of extraction of Am(III), Sr(II) and U(VI) from aqueous HNO₃ solutions by o-xylene solutions of P,P'-di(2-ethylhexyl) methylene- (H₂DEH[MDP]), ethylene- (H₂DEH[EDP]), and butylene- (H₂DEH[BuDP]) diphosphonic acids has been studied by the temperature coefficient method in the 25.0 to 60.0 °C range. Both extractant aggregation and extraction stoichiometries did not change with temperature. The extraction of Am(III) by H₂DEH[MDP], and that of U(VI) by all three extractants are strongly driven by both enthalpy and entropy variations. The extraction of Sr(II) by H₂DEH[MDP] is enthalpy driven. The extraction of Am(III) by H₂DEH[EDP] and H₂DEH[BuDP] is mainly driven by entropy changes. The extraction of Sr(II) by H₂DEH[EDP] and H₂DEH[BuDP] is characterized by an unfavorable entropy change and is not indicative of a micellar-type extraction mechanism.

INTRODUCTION

P,P'-di(2-ethylhexyl) alkylenediphosphonic acids have been proposed for actinide separation and pre-concentration procedures [1]. In Structure I, n is one, two or four, for P,P'-di(2-ethylhexyl) methylene- (H₂DEH[MDP]), ethylene- (H₂DEH[EDP]), and butylene- (H₂DEH[BuDP]) diphosphonic acid, respectively. Solvent extraction reagents containing the diphosphonic acid group, the solvent extraction equivalent of the Diphonix® resin [2], exhibit extraordinary affinity for tri-, tetra- and hexavalent actinides [3-5].

In toluene solutions H₂DEH[MDP] exists as dimers [6], H₂DEH[EDP] as hexamers [7], while H₂DEH[BuDP] exists mainly as trimeric aggregates [5]. The effect of these aggregation states on metal extraction has been reported in previous works [3-5]. Extractant dependencies higher than one were measured for the extraction of Am(III), Sr(II) and U(VI) by either H₂DEH[MDP] or H₂DEH[BuDP]. However, with H₂DEH[EDP], extractant dependencies equal to unity were reported for these ions
indicating that, with H₂DEH[EDP], extraction probably takes place through a micellar-type mechanism similar to other highly aggregated extraction systems [8-10].

\[
\begin{align*}
\text{H}_2\text{DEH}\text{[EDP]} & \\
\text{H}_2\text{DEH}\text{[MDP]} & \\
\text{H}_2\text{DEH}\text{[BuDP]} & \\
\end{align*}
\]

Structure 1

The objective of this work was to gain information on the thermodynamics of metal solvent extraction by the di(2-ethylhexyl) alkylenediphosphonic acids, by using the method of the temperature coefficient of the metal distribution ratio. Given the pronounced differences in extraction processes and type of metal species formed in the organic phase, it was reasonable to expect that the extraction of metal ions by H₂DEH[MDP], H₂DEH[EDP] and H₂DEH[BuDP] should be accompanied by different enthalpic and entropic contributions to the overall stability of the species formed.

EXPERIMENTAL

²⁴¹Am and ²³³U were obtained from ANL stocks. ⁸⁵Sr was obtained from Isotope Products Laboratories (Burbank, CA). The extractants were prepared and purified as described in previous works [3-5]. All other reagents were of analytical grade.

The aggregation of the extractants in toluene at various temperatures was measured by vapor pressure osmometry (VPO) using a Jupiter Model 833 vapor pressure osmometer as described previously [5-7,11]. The extractant solutions used for the VPO measurements were first equilibrated with appropriate nitric acid solutions in order to run the VPO measurements under conditions similar to those used for distribution ratio measurements. The distribution ratios, D, defined as the ratio of metal concentrations in the organic and aqueous phase, were measured following the procedure reported earlier [11]. The measured molar D values were converted to molal values by multiplying them by the appropriate aqueous to organic phase density ratio.

RESULTS AND DISCUSSIONS

Aggregation

The aggregation state of the extractants redetermined at temperatures up to 60°C confirmed the results of previous studies at 25°C for concentrations up to about 0.1 M, i.e., H₂DEH[MDP] is dimeric, H₂DEH[EDP] is hexameric, and H₂DEH[BuDP] is predominantly trimeric in toluene [5-7]. The details of the VPO results and data treatment are reported elsewhere [11].

Extraction Equilibria

The extraction stoichiometries of the target ions by the extractants at ambient temperature have previously been determined [3-5]. Although the extractant aggregation did not change in the 25 to 60 °C temperature range, it was necessary to redetermine the extraction stoichiometries at various temperatures. The temperature coefficient method for the determination of thermodynamic parameters is based on the assumption that the same
equilibria are operative in the temperature range of interest. If the extraction equilibria were
different at different temperatures, the temperature coefficient method would not be
applicable and calorimetric measurements would be required. The acid dependencies for
the three reactants were always equal to the formal charges of the metal cation being
extracted. The extractant dependencies were essentially the same as those previously
reported at room temperature [3-5] and are summarized in Table 1.

Table 1. Extractant dependencies in the 25 to 60 °C temperature range

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Am(III)</td>
<td>2.0</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>2.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>U(VI)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The extraction equilibrium of americium by the dimeric H₂DEH[MDP] can be written as:

\[ \text{Am}^{3+} + 2 (H₂A)_₂ ⇌ \text{Am}(H₅A₄) + 3 H^+ \]  

(1)

where H₂A stands for the diphosphonic acid and the bar indicates organic phase species.
Similar equations can be written for the other extractants and metal ions using the values of
the extractant (Table 1) and acid dependencies determined experimentally. By neglecting
aqueous phase nitrate ion complexation [12], the thermodynamic equilibrium constant for
the exemplificative case of the Am(III)-H₂DEH[MDP] system can be written as:

\[ K_{\text{Am,MDP}} = 4D \left[ \frac{[H^+]^3 \gamma_{\text{HNO}_3}^6}{C_{H₂A}^2 \gamma_{\text{Am,HN}}^4} \right] \]  

(2)

where D is the molal distribution ratio, \( \gamma_{\text{HNO}_3} \) and \( \gamma_{\text{Am,HN}} \) are the mean ionic molal activity
coefficients of HNO₃ and Am\((\text{NO}_3)_3\), respectively, and \( C_{H₂A} \) is the molal analytical
concentration of the extractant. Corresponding extraction equilibria and equilibrium
constant expressions can also be written for the hexameric H₂DEH[EDP] and the trimeric
H₂DEH[BuDP], as well as for Sr(II) and U(VI) extraction by the three extractants. The mean
molal activity coefficients of americium (europium was used as a stand-in), strontium and
uranyl nitrates at tracer concentration level in solutions of HNO₃ at the relevant ionic
strengths were calculated according to the method of Kusik and Meissner [13]. Other
details of the equilibrium constants calculations can be found elsewhere [14]. The values of
the thermodynamic equilibrium constant calculated at different temperatures are given in
Table 2.

Table 2. Equilibrium constants for the extraction of Am(III), Sr(II) and U(VI) by
H₂DEH[MDP], H₂DEH[EDP] and H₂DEH[BuDP] in o-xylene.

<table>
<thead>
<tr>
<th>T °C</th>
<th>logK Am(III)</th>
<th>logK Sr(II)</th>
<th>logK U(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MDP EDP BuDP</td>
<td>MDP EDP BuDP</td>
<td>MDP EDP BuDP</td>
</tr>
<tr>
<td>25</td>
<td>8.82 4.67 1.49</td>
<td>1.80 -1.17 -2.21</td>
<td>5.63 7.31 5.06</td>
</tr>
<tr>
<td>30</td>
<td>8.78 4.66 1.50</td>
<td>1.78 -1.22 -2.16</td>
<td>5.54 7.23 5.01</td>
</tr>
<tr>
<td>35</td>
<td>8.75 4.68 1.54</td>
<td>- - -</td>
<td>5.54 7.14 4.96</td>
</tr>
<tr>
<td>40</td>
<td>8.71 4.66 1.54</td>
<td>1.70 -1.32 -2.17</td>
<td>5.38 7.07 4.92</td>
</tr>
<tr>
<td>45</td>
<td>8.68 4.66 1.58</td>
<td>1.67 -1.38 -2.19</td>
<td>5.32 7.00 4.88</td>
</tr>
<tr>
<td>50</td>
<td>8.65 4.66 1.59</td>
<td>1.64 -1.42 -2.16</td>
<td>5.22 6.93 4.83</td>
</tr>
<tr>
<td>60</td>
<td>8.59 4.64 1.67</td>
<td>1.58 -1.50 -2.15</td>
<td>5.10 6.78 4.76</td>
</tr>
</tbody>
</table>
The uncertainties in these equilibrium constant values (in log units), estimated from the statistical analysis of the logK data, are 0.05 for americium, 0.03 for strontium, and 0.08 for uranium, respectively. The logK values clearly reflect the fact that H2DEH[MDP] has the highest extraction efficiency for the three metal ions (except for U(VI)) and H2DEH[BuDP] the least [3-5].

**Free Energy, Enthalpy and Entropy Variations**

The enthalpy and entropy changes of the extraction processes were calculated from the slopes (=ΔH°/2.303R) and intercepts (=ΔS°/2.303R), respectively, of the plots of logK vs. 1/T, with R = 8.314 JK⁻¹mol⁻¹. Previously discussed conditions regarding the constancy of ΔH° and aqueous phase activity coefficients over the temperature range investigated apply here as well [15-17]. Plots of logK for each metal ion vs. 1/T are shown in Figure 1.

*Figure 1. Effect of temperature on the extraction of Am(III), Sr(II) and U(VI) from aqueous HNO₃ by H₂DEH[MDP], H₂DEH[EDP] and H₂DEH[BuDP] in o-xylene.*

The ΔH° and ΔS° values calculated from the plots, along with the ΔG° values calculated from ΔG° = -2.303RTlogK are given in Table 3. The uncertainties reported for ΔH° and ΔS° are the standard errors of the slopes and intercepts, respectively. Those for ΔG° were obtained from the standard error of logK.

In the extraction of a metal cation by a liquid cation exchanger, the net enthalpy and entropy variations of the extraction reaction are the result of several different processes. The dehydration of the metal cation generally involves a positive enthalpy variation (ΔH > 0) as a result of the breakage of ion-water bonds, and a positive entropy variation (ΔS > 0) due to an increase of disorder in the system. The opposite will occur for the hydration of the proton. On the other hand, metal coordination by the organic ligand will result in a negative enthalpy variation (ΔH < 0), as a consequence of replacing relatively weak hydrogen bonds with stronger metal coordination bonds, and in a negative entropy variation (ΔS < 0) due to the increase of order caused by the new bonds. The deprotonation of the extractant will produce opposite effects.
Table 3: Thermodynamic parameters for the extraction of Am(III), Sr(II) and U(VI) by H₂DEH[MDP], H₂DEH[EDP] and H₂DEH[BuDP] in o-xylene.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Extractant</th>
<th>ΔG° at 25 °C kJ/mol</th>
<th>ΔH° at 25 °C kJ/mol</th>
<th>ΔS° at 25 °C J/mol/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am(III)</td>
<td>H₂DEH[MDP]</td>
<td>-50.3 ± 0.1</td>
<td>-12.5 ± 0.2</td>
<td>127 ± 1</td>
</tr>
<tr>
<td></td>
<td>H₂DEH[EDP]</td>
<td>-26.7 ± 0.5</td>
<td>-1.4 ± 0.5</td>
<td>85 ± 2</td>
</tr>
<tr>
<td></td>
<td>H₂DEH[BuDP]</td>
<td>-8.5 ± 0.7</td>
<td>9.5 ± 0.9</td>
<td>60 ± 4</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>H₂DEH[MDP]</td>
<td>-10.3 ± 0.1</td>
<td>-12.3 ± 0.4</td>
<td>-7 ± 1</td>
</tr>
<tr>
<td></td>
<td>H₂DEH[EDP]</td>
<td>6.7 ± 0.3</td>
<td>-18.2 ± 0.4</td>
<td>-84 ± 2</td>
</tr>
<tr>
<td></td>
<td>H₂DEH[BuDP]</td>
<td>12.6 ± 0.2</td>
<td>2 ± 1</td>
<td>-35 ± 4</td>
</tr>
<tr>
<td>U(VI)</td>
<td>H₂DEH[MDP]</td>
<td>-32.2 ± 0.5</td>
<td>-30 ± 2</td>
<td>8 ± 2</td>
</tr>
<tr>
<td></td>
<td>H₂DEH[EDP]</td>
<td>-41.7 ± 0.6</td>
<td>-29 ± 1</td>
<td>44 ± 3</td>
</tr>
<tr>
<td></td>
<td>H₂DEH[BuDP]</td>
<td>-28.9 ± 0.3</td>
<td>-16 ± 1</td>
<td>42 ± 2</td>
</tr>
</tbody>
</table>

Among the ions investigated, Am(III) behaves in a way which is easier to rationalize based on the arguments outlined above. The ΔH° values for Am(III) extraction exhibit a trend along the H₂DEH[MDP], H₂DEH[EDP], H₂DEH[BuDP] series, with the reaction being exothermic for the first, thermoneutral for the second, and endothermic for the third extractant, respectively. The trend in ΔH° can be interpreted as arising from the formation of progressively less stable chelate rings along the diphosphonic acids series, as the length of the alkyl chain separating the two phosphorus atoms of the molecule increases. A favorable enthalpic term is observed only for Am(III) extraction by H₂DEH[MDP], a ligand with which the metal can form several highly stable six-membered chelate rings. In all cases, the extraction is facilitated by a favorable entropic term, as typically observed for the formation of chelate complexes [18]. The almost zero or positive enthalpy variation with a concomitant favorable entropy variation confirm for H₂DEH[EDP] and for H₂DEH[BuDP] a micellar-like type of extraction process [15,19]. The diphosphonic acids form organic phase aggregates characterized by highly ordered structures. When the metal ion is transferred to the organic phase, it becomes part of these structures adding little order to the system. Consequently, the entropy variation is mainly determined by the disorder generated by the metal ion dehydration.

The extraction of Sr(II) by H₂DEH[MDP] is enthalpy driven. With H₂DEH[EDP] and H₂DEH[BuDP], Sr(II) extraction is very inefficient, as indicated by the positive values of ΔG°, as a result of strongly unfavorable entropic terms. The H₂DEH[EDP] results are indicative of strong metal-ligand coordination and attendant increased ordering. The negative entropic terms for all three extractants also suggest that the hydration of the exchanged protons predominates over the dehydration of the metal ion. Overall, in the extraction of Sr(II) by the three diphosphonic acids, the enthalpy and entropy changes do not lend themselves to indicate a micellar-type extraction mechanism.

The extraction of U(VI) by all three extractants is strongly driven by both enthalpy and entropy variations, which testifies to the extremely high affinity exhibited especially by H₂DEH[MDP] and H₂DEH[EDP] for U(VI). The negative enthalpy change associated with metal coordination predominates over the other opposing enthalpic factors. The increasing ΔS° values observed for U(VI) extraction in moving from H₂DEH[MDP] to the other extractants may be due, at least in part, to the overlapping of a solvation mechanism with the ion-exchange mechanism. Extraction of uranyl nitrate by alkylphosphoric acids as solvated complexes at relatively high aqueous acidities is well-known [20], and has been reported for alkylatediphosphonic acids as well [3-5]. In a solvation mechanism, the neutral salt is transferred into the organic phase without simultaneous transfer of protons in the
other direction. Consequently, the positive entropy variation associated with the dehydration of the extracted cation and anions dominates the net entropy variation. A solvation mechanism is more likely for extractants having a more basic P=O group as observed along the \( \text{H}_2\text{DEH}\{\text{MDP} \}, \text{H}_2\text{DEH}\{\text{EDP} \}, \text{H}_2\text{DEH}\{\text{BuDP} \} \) series (21), and would therefore explain the \( \Delta S^\circ \) trend reported for U(VI) in Table 2.

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