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

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To cite this Article Otu, E. O. and Chiarizia, R.(2003) 'Temperature Effect On The Extraction Of Am(iii), U(vi), And Sr(ii) By Dialkyl-substituted Alkylenediphosphonic Acids', Separation Science and Technology, 38: 12, 2619 — 2636
To link to this Article: DOI: 10.1081/SS-120022563
URL: http://dx.doi.org/10.1081/SS-120022563

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, Nos. 12 & 13, pp. 2619–2636, 2003

Temperature Effect on the Extraction of Am(III), U(VI), and Sr(II) by Dialkyl-Substituted Alkylenediphosphonic Acids[#]

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ABSTRACT

Solvent extraction reagents containing the diphosphonic acid group exhibit extraordinary affinity for tri-, tetra-, and hexavalent actinides. Use of these reagents has been proposed for actinide separation and preconcentration procedures. A new extractant, P,P′-di(2-ethylhexyl) benzene-1,2-diphosphonic acid (H_2DEH[1,2-BzDP]), has been synthesized. Its metal extraction characteristics are reported and compared to the previously synthesized P,P′-di(2-ethylhexyl) methylene-(H_2DEH[MDP]), ethylene-(H_2DEH[EDP]), and

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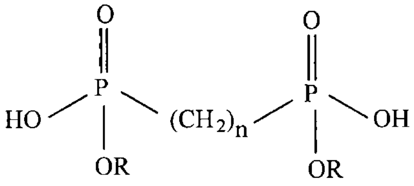
DOI: 10.1081/SS-120022563
0149-6395 (Print); 1520-5754 (Online)
Published by Marcel Dekker, Inc.
www.dekker.com

butylene-(H_2DEH[BuDP]) diphosphonic acids. Different degrees of aggregation and different extraction mechanisms and stoichiometries have been reported for these ligands.

In this work, thermodynamic parameters associated with the extraction of selected metal ions by these ligands were measured to provide further insight into the mechanism of the extraction processes involved. Knowledge of the enthalpy, entropy, and free-energy changes, in combination with other fundamental principles governing extraction of metal ions by these ligands will increase their usefulness in liquid–liquid extraction. Thermodynamic parameters of the extraction process were determined by the temperature dependence of the distribution ratio in the temperature range of 25 to 60°C. Neither the aggregation state of the free ligands nor the extraction stoichiometries at trace metal concentration level change in the whole range of temperatures investigated. The effect of temperature on the extraction of ^{241}Am, ^{233}U, and ^{85}Sr from HNO_3 solutions by *o*-xylene solutions of the extractants are reported.

INTRODUCTION

A general formula for some previously developed solvent extraction reagents of the P,P′-di(alkyl) alkylenediphosphonic acid type is shown in Structure I, where R is the 2-ethylhexyl group, and n is 1, 2, or 4, for P,P′-di(2-ethylhexyl) methylene-(H_2DEH[MDP]), ethylene-(H_2DEH[EDP]), and butylene-(H_2DEH[BuDP]) diphosphonic acid, respectively.



Structure I

The length of the alkylene chain separating the two P atoms of the extractant molecule affects the aggregation state of the extractant. In toluene, H_2DEH[MDP] is dimeric, while H_2DEH[EDP] forms hexameric, spherical aggregates and H_2DEH[BuDP] exists predominantly in the form of trimeric aggregates.[1–6]

As part of our ongoing work with diphosphonic acids, we are studying new compounds, the P,P′-di(2-ethylhexyl) benzene-diphosphonic acids, where the benzene ring bridges the two phosphorus centers. We synthesized and characterized P,P′-di(2-ethylhexyl) benzene-1,2-diphosphonic acid, H_2DEH[1,2-BzDP].

Based on the separation between the two phosphorus atoms, H_2DEH[1,2-BzDP] can be compared to H_2DEH[EDP]. However, the rigidity introduced in H_2DEH[1,2-BzDP] by the benzene ring could make it behave more like H_2DEH[MDP]. Because of this rigidity, it was expected that H_2DEH[1,2-BzDP] would behave more similarly to H_2DEH[MDP] than H_2DEH[EDP]. The synthesis, characterization, and metal extraction characteristics of P,P′-di(2-ethylhexyl) benzene-1,3-diphosphonic acid and P,P′-di(2-ethylhexyl) benzene-1,4-diphosphonic acid isomers are currently under study. These diphosphonic acids have the phosphorus centers preorganized for metal extraction. This should reflect in their metal solvent extraction chemistry.

Solvent extraction reagents containing the diphosphonic acid group, the solvent extraction equivalent of the Diphonix resin,[7] exhibit extraordinary affinity for tri-, tetra-, and hexavalent actinides. Use of these reagents was proposed for actinide separation and preconcentration procedures.[8] The effect of the aggregation state of the di(2-ethylhexyl) alkylenediphosphonic acids on their metal solvent extraction chemistry was investigated in some detail.[6,9–11] The extractant and acid dependencies for the extraction of Am(III), U(VI), and Sr(II) by these extractants have also been reported. Based on these previous works, it is known that metal–ion extraction processes and the type of metal–extractant complexes formed in the organic phase are different for the acids investigated.

With H_2DEH[MDP], ions transfer from the aqueous to the organic phase to become part of a complex involving two extractant dimers and a large number of chelate rings (four 6-membered and three 8-membered rings).[4,10] For this type of bonding to occur, it is likely that complete dehydration of the cation is required. In the case of H_2DEH[EDP], where the extraction process is reminiscent of a micellar extraction, the metal cation can be transferred into the organic phase as hexameric aggregates retaining some of its water of hydration.[9] Furthermore, the chelate rings formed through coordination of the metal to the P═O and POO^- groups of the extractant should be 7- and 8-membered, respectively. Therefore, they are less stable than in the H_2DEH[MDP] case. With H_2DEH[BuDP], interaction of the cation with the extractant trimers included in the complex should only involve formation of very large and unstable chelate rings.[6]

Given the pronounced differences in extraction processes and type of metal species formed in the organic phase, it seems reasonable to expect that the extraction of metal ions by H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP] should be accompanied by different enthalpic and entropic contributions to the overall stability of the species formed.

The objective of this work was to gain information on the thermodynamics of metal-solvent extraction by the di(2-ethylhexyl) diphosphonic acids, by using the method of the temperature coefficient of the metal distribution ratio. The enthalpy and entropy changes upon metal complexation should shed further light on the metal extraction processes. The extraction of Am(III) and Sr(II) by P,P′-di(2-ethylhexyl) benzene-1,2-diphosphonic acid, H_2DEH[1,2-BzDP], are reported and compared with previous results with the di(2-ethylhexyl) alkylenediphosphonic acids. Although U(VI) data with H_2DEH[1,2-BzDP] are not available, results with H_2DEH[MDP], H_2DEH[EDP] and H_2DEH[BuDP] are included for a fuller comparison among the di(2-ethylhexyl) diphosphonic acids.

EXPERIMENTAL

Materials

Freshly prepared ^{233}U and ^{241}Am were obtained from ANL stocks. ^{85}Sr was obtained from Isotope Products Laboratories (Burbank, CA). The extractants were prepared and purified as described in previous works.[6,9,10] Extractant solutions were prepared by dissolving weighed amounts of the extractants in *o*-xylene (HPLC grade, Aldrich Chemical Co., Milwaukee, WI). The extractant concentrations were in the 10^{-3} to 10^{-1} M range. Tracer level aqueous metal ion concentration solutions were prepared using Ultrex reagent nitric acid (J.T. Baker Chemical Co. Sanford, ME, USA) and water from a Milli-Q2 purification system. The aqueous phase nitric acid concentrations varied in the range 0.01 to 7 M.

Procedures

Aggregation Measurements

The aggregation of H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP] in toluene (a more convenient diluent than *o*-xylene for VPO measurements) at various temperatures was measured by vapor pressure osmometry (VPO) using a Jupiter Model 833 vapor pressure osmometer as described previously.[2] The instrument was calibrated at each temperature of interest using toluene solutions of sucrose octaacetate as the monomeric standard. The aggregation measurements of H_2DEH[1,2-BzDP] were studied in a similar manner, and the details are reported elsewhere.[12]

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.[13] Duplicate extractions were performed at various temperatures, and duplicate analyses were performed on the separated phases. These duplicate experiments were used to estimate the uncertainty levels in the distribution ratio measurements. Although the uncertainty interval was substantially higher for D values greater than 10^3, the reproducibility of the D measurements was within 5%. 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

To employ the extraction coefficients as a function of temperature for the determination of thermodynamic parameters (as in this study), it was necessary to ascertain that the same equilibria are operative in the temperature range of interest. It is conceivable that the extractants aggregation might change as a function of temperature, which might result in a change of the metal ion extraction stoichiometry. Vapor pressure osmometric measurements were performed on toluene solutions of the extractants.

The results for the alkylene diphosphonic acids, reported in detail previously,[13] showed that the aggregation state of the extractants did not change in the 25.0 to 60.0°C temperature range (i.e., H_2DEH[MDP] remains dimeric; H_2DEH[EDP] is essentially hexameric; and H_2DEH[BuDP] exists primarily as trimeric aggregates $[\beta_3 = (1.4 \pm 0.2) \times 10^5]$ in equilibrium with low concentrations of hexameric aggregates $[\beta_6 = (1.3 \pm 0.2) \times 10^{11})]$.

The benzene diphosphonic acid solution in toluene exhibited a characteristic aggregation behavior. The results are reported in detail elsewhere.[12] In the 25 to 60°C temperature range, the VPO measurements for freshly prepared solutions of H_2DEH[1,2-BzDP] indicated that the ligand exists predominantly as a dimer in toluene, similar to H_2DEH[MDP]. However, upon standing for about 2 weeks, precipitation occurred in both the toluene solutions and in the *o*-xylene solutions used for metal extraction. This phenomenon was not observed with the alkylenediphosphonic acids. To establish the aggregation of the extractant in the solution to be used for metal extraction, the *o*-xylene was removed from the filtrate under nitrogen, and the oily residue was taken up in toluene and dilutions made for VPO measurements. The VPO results indicated that the aged extractant is monomeric. This instability exhibited by H_2DEH[1,2-BzDP] is the subject of another study that is underway. It is relevant for this work, however, that the degree of aggregation of aged H_2DEH[1,2-BzDP] was not affected by temperature and remained unchanged in the concentration range studied, as observed for the alkylenediphosphonic acids.

Extraction Equilibria

The extraction stoichiometries of the target metal ions [Am(III), Sr(II), and U(VI)] at room temperature were determined previously using *o*-xylene as the diluent.[6,9,10,12] Although the extractant aggregation did not change in the 25.0 to 60.0°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 condition 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 slopes of the acid dependencies are -3 for Am(III) and -2 for Sr(II) and U(VI), with all four extractants. These correspond to the negative values of the formal charge of the metal ions, indicating that three or two protons are always displaced from the organic phase ligands upon extraction of Am^{3+} and Sr^{2+} or UO_2^{2+}, respectively. The acid dependencies at various temperatures were reported previously.[12–14] With U(VI) and H_2DEH[EDP], however, an acid dependency slope of -2 was observed only in a small range of aqueous acidity, indicating that other extraction mechanisms, such as solvation, are possible. For the U(VI)-H_2DEH[EDP] system, therefore, the thermodynamic considerations of this article apply only in the limited set of conditions where an ideal ion exchange stoichiometry applies.

The extractant dependencies in the temperature range of this study were previously reported.[12–14] The extractant dependencies for all the investigated systems, in the low aqueous phase acid region where ion-exchange mechanism predominates, are summarized in Table 1.

The slopes of 2 and 3 for Am(III) and Sr(II) when H_2DEH[1,2-BzDP] is the extractant indicate that these metal ions are coordinated to two and three monomeric extractant molecules, respectively. Extractant dependencies of 2 for Am(III) and Sr(II) and 1 for U(VI) when H_2DEH[MDP] is the extractant indicate that these metal ions are coordinated in the organic phase to two dimers and one dimer of the ligand, respectively. The unity extractant dependency for all metal ions when H_2DEH[EDP] is the ligand indicates that extraction may take place through a micellar-type mechanism. This is similar to other highly aggregated

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

Ion	H_2DEH[1,2BzDP]	H_2DEH[MDP]	H_2DEH[EDP]	H_2DEH[BuDP] trimer
Am(III)	3.0	2.0	1.0	1.5
Sr(II)	2.0	2.0	1.0	2.0
U(VI)	ND	1.0	1.0	1.0

ND = Not determined.

extraction systems, such as dinonylnaphthalene- and didodecylnaphthalenesulfonic acids,[15–17] mono(2-ethylhexyl) phosphoric acid,[18–20] and quaternary alkylammonium salts,[21] wherein cations are extracted into the core of the extractant aggregate. The fractional value observed for Am(III) with H_2DEH[BuDP] indicates the coexistence in the *o*-xylene phase of complexes in which Am(III) is bound to one and two H_2DEH[BuDP] trimers, respectively. Sr(II) coordinates to two trimers, while U(IV) coordinates to one trimer.

In all cases, the extraction reactions remained essentially the same in the whole temperature range, although the effect of temperature on the extraction of the individual metal ions by the three extractants is remarkably different. The extraction of Am(III) and Sr(II) decreases as temperature increases for H_2DEH[1,2-BzDP] and H_2DEH[MDP]. The extractability of Am(III) by H_2DEH[EDP] is essentially not affected by temperature, whereas the extraction reaction is endothermic with H_2DEH[BuDP]. The extraction of Sr(II) decreases as temperature increases when H_2DEH[EDP] is the extractant. There is essentially no change in the extraction of Sr(II) by H_2DEH[BuDP] as a function of temperature. The extraction of U(VI) decreases as temperature increases along the series H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP]. The extraction of U(VI) by H_2DEH[1,2-BzDP] was not studied.

Equilibrium Constants

Based on the acid and extractant dependencies, the extraction equation for Am(III) by the monomeric H_2DEH[1,2-BzDP] can be written as:

$$\mathrm{Am}^{3+} + 3(\overline{\mathrm{H_2A}}) \Leftrightarrow \overline{\mathrm{Am(H_3A_3)}} + 3\mathrm{H}^+ \tag{1}$$

where H_2A stands for the diphosphonic acid, species with the bar exist in the organic phase, and charged species exist in the aqueous phase.

The thermodynamic equilibrium constant can be written as:

$$K_{Am,BzDP} = \frac{[\overline{Am(H_3A_3)}]}{[Am^{3+}]} \frac{[H^+]^3}{C^3_{H_2A}} \frac{\gamma^6_{\pm,HN}}{\gamma^4_{\pm,AN}} \tag{2}$$

where $\gamma_{\pm,\mathrm{HN}}$ and $\gamma_{\pm,\mathrm{AN}}$ are the mean molal ionic activity coefficients of HNO_3 and $Am(NO_3)_3$, respectively, and C_{H2A} is the molal concentration of the extractant.

When nitrate complexing of the target metal ions in aqueous nitric acid medium is taken into account, the following equation can be written in the case of Am(III):

$$\mathrm{Am}^{3+} + \mathrm{iNO_3}^- \Leftrightarrow \mathrm{Am(NO_3)_i}^{3-\mathrm{i}} \tag{3}$$

The total concentration of Am(III) in the aqueous phase, $[Am^{3+}]_{tot}$, can be shown to be

$$[Am^{3+}]_{tot} = [Am^{3+}] \times \left(1 + \frac{\beta_1 \gamma_{Am^{3+}} [NO_3^-] \gamma_{NO_3^-}}{\gamma_{Am(NO_3)^{2+}}} + \frac{\beta_2 \gamma_{Am^{3+}} [NO_3^-]^2 \gamma^2_{NO_3^-}}{\gamma_{Am(NO_3)_2^+}}\right) \tag{4}$$

where β is the formation constant for the nitrate complexes. Recognizing that the distribution ratio, D, is the ratio of the concentration of metal in the organic phase and the total concentration of metal in the aqueous phase, and introducing mean molal activity coefficients of the species in eq. (4), eq. (2) can be expressed as:

$$K_{Am,BzDP} = D \frac{[H^+]^3 \gamma^6_{\pm,HN}}{C^3_{H_2A}} \left(\frac{1}{\gamma^4_{\pm,AN}} + \frac{\beta_1 [NO_3^-]}{\gamma^3_{\pm,AN}} + \frac{\beta_2 [NO_3^-]^2}{\gamma^2_{\pm,AN}}\right) \tag{5}$$

The extraction equilibria of Am(III) by the dimeric H_2DEH[MDP], hexameric H_2DEH[EDP], and trimeric H_2DEH[BuDP] are given by eqs. (6, through 8), respectively:

$$\mathrm{Am}^{3+} + 2(\overline{\mathrm{H_2A}})_2 \Leftrightarrow \overline{\mathrm{Am(H_5A_4)}} + 3\mathrm{H}^+ \tag{6}$$

$$\mathrm{Am}^{3+} + (\overline{\mathrm{H_2A}})_6 \Leftrightarrow \overline{\mathrm{Am(H_9A_6)}} + 3\mathrm{H}^+ \tag{7}$$

$$\mathrm{Am}^{3+} + 1.5(\overline{\mathrm{H_2A}})_3 \Leftrightarrow \overline{\mathrm{Am(H_6A_{4.5})}} + 3\mathrm{H}^+ \tag{8}$$

Proceeding as for H_2DEH[1,2-BzDP], the corresponding thermodynamic equilibrium constant expressions can be written as follows:

$$K_{Am,MDP} = 4\,D\frac{[H^+]^3\gamma^6_{\pm,HN}}{C^2_{H_2A}}\left(\frac{1}{\gamma^4_{\pm,AN}} + \frac{\beta_1[NO_3^-]}{\gamma^3_{\pm,AN}} + \frac{\beta_2[NO_3^-]^2}{\gamma^2_{\pm,AN}}\right) \tag{9}$$

$$K_{Am,EDP} = 6\,D\frac{[H^+]^3\gamma^6_{\pm,HN}}{C_{H_2A}}\left(\frac{1}{\gamma^4_{\pm,AN}} + \frac{\beta_1[NO_3^-]}{\gamma^3_{\pm,AN}} + \frac{\beta_2[NO_3^-]^2}{\gamma^2_{\pm,AN}}\right) \tag{10}$$

$$K_{Am,BuDP} = D\frac{[H^+]^3\gamma^6_{\pm,HN}}{[(H_2A)_3]^{1.5}}\left(\frac{1}{\gamma^4_{\pm,AN}} + \frac{\beta_1[NO_3^-]}{\gamma^3_{\pm,AN}} + \frac{\beta_2[NO_3^-]^2}{\gamma^2_{\pm,AN}}\right) \tag{11}$$

The concentration of the trimeric species to be used in eq. (11) can be calculated for each analytical concentration of H_2DEH[BuDP] using the β_3 and β_6 reported earlier. Equations (8 and 11) involve the approximation that Am(III) (and the other metal ions) are extracted only by trimeric H_2DEH[BuDP]. In reality, metal extraction by monomeric and hexameric extractant molecules in equilibrium with the trimer cannot be excluded a priori. The approximation should be valid, however, since the trimeric aggregate is always the predominant species under the conditions of this work.[6,13]

Following the same procedure, the thermodynamic equilibrium constant expressions for Sr(II) and U(VI) can be written as follows:

$$K_{Sr,BzDP} = D\frac{[H^+]^2\gamma^4_{\pm,HN}}{C^2_{H_2A}}\left(\frac{1}{\gamma^3_{\pm,AN}} + \frac{\beta_1[NO_3^-]}{\gamma^2_{\pm,AN}} + \beta_2[NO_3^-]^2\right) \tag{12}$$

$$K_{Sr,MDP} = 4\,D\frac{[H^+]^2\gamma^4_{\pm,HN}}{C^2_{H_2A}}\left(\frac{1}{\gamma^3_{\pm,SN}} + \frac{\beta_1[NO_3^-]}{\gamma^2_{\pm,SN}} + \beta_2[NO_3^-]^2\right) \tag{13}$$

$$K_{Sr,EDP} = 6\,D\frac{[H^+]^2\gamma^4_{\pm,HN}}{C_{H_2A}}\left(\frac{1}{\gamma^3_{\pm,SN}} + \frac{\beta_1[NO_3^-]}{\gamma^2_{\pm,SN}} + \beta_2[NO_3^-]^2\right) \tag{14}$$

$$K_{Sr,BuDP} = D\frac{[H^+]^2\,\gamma^4_{\pm,HN}}{[(H_2A)_3]^2}\left(\frac{1}{\gamma^3_{\pm,SN}} + \frac{\beta_1[NO_3^-]}{\gamma^2_{\pm,SN}} + \beta_2[NO_3^-]^2\right) \tag{15}$$

$$K_{U,MDP} = 2\,D\frac{[H^+]^2\,\gamma^4_{\pm,HN}}{C_{H_2A}}\left(\frac{1}{\gamma^3_{\pm,UN}} + \frac{\beta_1[NO_3^-]}{\gamma^2_{\pm,UN}} + \beta_2[NO_3^-]^2\right) \qquad (16)$$

$$K_{U,EDP} = 6\,D\frac{[H^+]^2\,\gamma^4_{\pm,HN}}{C_{H_2A}}\left(\frac{1}{\gamma^3_{\pm,UN}} + \frac{\beta_1[NO_3^-]}{\gamma^2_{\pm,UN}} + \beta_2[NO_3^-]^2\right) \qquad (17)$$

$$K_{U,BuDP} = D\frac{[H^+]^2\,\gamma^4_{\pm,HN}}{[(H_2A)_3]}\left(\frac{1}{\gamma^3_{\pm,UN}} + \frac{\beta_1[NO_3^-]}{\gamma^2_{\pm,UN}} + \beta_2[NO_3^-]^2\right) \qquad (18)$$

where $\gamma_{\pm,\mathrm{SN}}$ and $\gamma_{\pm,\mathrm{UN}}$ are the mean molal ionic activity coefficients of $Sr(NO_3)_2$ and $UO_2(NO_3)_2$, respectively.

The following β values were taken from the literature[22]: $\beta_1 = 1.82$ for Am(III), $\beta_1 = 6.3$ and $\beta_2 = 6.3$ for Sr(II), and $\beta_1 = 0.5$ for U(VI). The mean molal ionic activity coefficients of americium, (europium chloride was used as a stand-in), strontium, and uranyl nitrates at tracer concentration level in solutions of HNO_3 at the relevant ionic strengths were calculated according to the method of Kusik and Meissner.[23]

The values of the thermodynamic equilibrium constants calculated at different temperatures are given in Table 2. For these calculations, the variation of the activity coefficients with temperature was neglected. The uncertainties in these equilibrium constant values are for Am(III) 0.1 and for Sr(II) 0.13, 0.01, 0.05, and 0.03 log units for H_2DEH[1,2-BzDP], H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP], respectively; for U(VI) 0.08, 0.13, 0.06 log units for H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP], respectively. These uncertainties are the average standard errors estimated from statistical analysis of the log K data at each temperature for the different acid and ligand concentrations included in this study.

The K values in Table 2 clearly reflect the fact that the diphosphonic acids are very good extractants for the target metal ions [especially Am(III) and U(VI)], with the order being H_2DEH[1,2-BzDP] > H_2DEH[MDP] > H_2DEH[EDP] > H_2DEH[BuDP] for Am(III) and Sr(II), and H_2DEH[EDP] > H_2DEH[MDP] > H_2DEH[BuDP] for U(VI). The ordering for the alkylenediphosphonic acids is similar to previous reports at room temperature.[6,9,10]

It should be noted that neglecting nitrate complexation of the metal ions in the aqueous phase would yield values that are only 2 to 5% lower than those reported in Table 2 and would not affect the discussion of the efficiency of these extractants and the conclusions about the thermodynamic parameters controlling the extraction process for the extractants.

Table 2. Thermodynamic equilibrium constants for the extraction of Am(III), Sr(II), and U(VI) by H_2DEH[1,2-BzDP], H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP] in *o*-xylene.

	Log K Am(III)				log K Sr(II)				log K U(VI)		
T (°C)	BzDP	MDP	EDP	BuDP	BzDP	MDP	EDP	BuDP	MDP	EDP	BuDP
25	12.65	9.26	4.80	1.52	1.76	1.84	− 1.13	− 2.17	5.80	7.52	5.16
30	12.47	9.22	4.79	1.53	1.70	1.82	− 1.18	− 2.12	5.71	7.45	5.11
35	—	9.19	4.81	1.57	—	—	—	—	5.62	7.35	5.06
40	12.14	9.16	4.80	1.57	1.55	1.74	− 1.28	− 2.13	5.55	7.28	5.02
45	—	9.13	4.80	1.61	—	1.71	− 1.34	− 2.15	5.49	7.21	4.98
50	11.74	9.09	4.79	1.62	1.39	1.68	− 1.38	− 2.12	5.39	7.14	4.93
60	11.29	9.03	4.77	1.70	1.25	1.62	− 1.46	− 2.11	5.27	6.99	4.86

Free Energy, Enthalpy, and Entropy Changes

The Gibbs–Helmholtz equation can be written in the form:

$$\log K = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \qquad (19)$$

where R (8.314 $JK^{-1}mol^{-1}$) is the gas constant. The enthalpy and entropy changes of the extraction processes were calculated from the slopes ($-\Delta H^0/2.303R$) and intercepts ($\Delta S^0/2.303R$), respectively, of the plots of logK vs $\frac{1}{T}$. Previously discussed conditions regarding the constancy of ΔH^0 and aqueous phase activity coefficients over the temperature range investigated apply here as well.[24–27] The plots of the average log K for each metal ion vs $\frac{1}{T}$ are shown in Fig. 1. The lines in these plots were obtained through the linear regression features of the program Origin (version 3.5, Microcal Software, Inc., Northampton, MA, USA).

The figure shows that the extraction of Am(III) is more exothermic for H_2DEH[1,2-BzDP] than for H_2DEH[MDP], thermoneutral for H_2DEH[EDP], and endothermic for H_2DEH[BuDP]. The extraction of Sr(II)

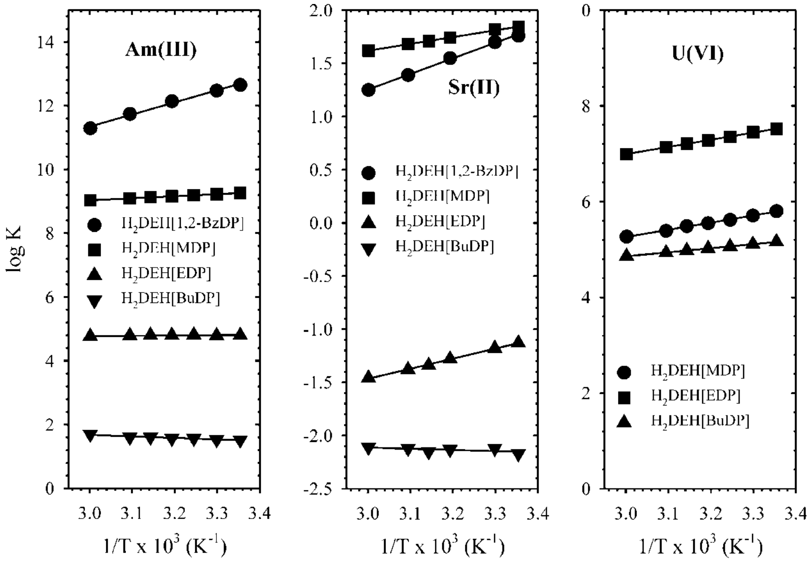


Figure 1. Effect of temperature on the extraction of AM(III), SR(II), and U(VI) from aqueous HNO_3 by H_2DEH[1,2-BzDP], H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP] in *o*-xylene.

is exothermic for $H_2DEH[1,2\text{-}BzDP]$, $H_2DEH[MDP]$, and $H_2DEH[EDP]$, and only slightly endothermic for $H_2DEH[BuDP]$. The extraction of U(VI) by the three alkylene diphosphonic acids is exothermic.

The ΔH^0 and ΔS^0 values calculated from the plots, along with the ΔG^0 values calculated from $\Delta G^0 = -2.303\,RT \log K$ are given in Table 3. The uncertainties reported for ΔH^0 and ΔS^0 are the standard errors of the slopes and intercepts, respectively. Those for ΔG^0 were obtained from the standard error of log K.

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 ($\Delta H > 0$) as a result of the breakage of ion–water bonds, and a positive entropy variation ($\Delta S > 0$) due to an increase of disorder in the system by the release of coordinated water. The opposite will occur for the hydration of the proton(s) lost by the ligand. On the other hand, metal coordination by the organic ligand will result in a negative enthalpy variation ($\Delta H < 0$), as a consequence of replacing relatively weak hydrogen bonds (typical of organophosphorus acids) with stronger metal coordination bonds, and in a negative entropy variation ($\Delta S < 0$), due to the increase of order caused by the new bonds. The deprotonation of the extractant produces opposite effects.

The trend in ΔH^0 can be interpreted as arising from the formation of progressively less stable chelate rings along this series. A favorable enthalpic

Table 3. Thermodynamic parameters for the extraction of Am(III), Sr(II), and U(VI) by $H_2DEH[1,2\text{-}BzDP]$, $H_2DEH[MDP]$, $H_2DEH[EDP]$, and $H_2DEH[BuDP]$ in *o*-xylene.

Ion	Extractant	ΔG^0 at 25°C kJ/mol	ΔH^0 kJ/mol	ΔS^0 at 25°C J/mol/K
Am(III)	$H_2DEH[1,2\text{-}BzDP]$	−72.4 ± 0.4	−73.0 ± 3.8	−2 ± 12
	$H_2DEH[MDP]$	−52.9 ± 0.6	−12.3 ± 0.3	136 ± 2
	$H_2DEH[EDP]$	−27.4 ± 0.6	−1.3 ± 0.7	88 ± 3
	$H_2DEH[BuDP]$	−8.7 ± 0.7	9.5 ± 0.9	61 ± 4
Sr(II)	$H_2DEH[1,2\text{-}BzDP]$	−10.1 ± 0.7	−27.9 ± 0.8	−60 ± 2
	$H_2DEH[MDP]$	−10.5 ± 0.1	−12.3 ± 0.4	−6 ± 1
	$H_2DEH[EDP]$	6.5 ± 0.3	−18.2 ± 0.4	−83 ± 2
	$H_2DEH[BuDP]$	12.4 ± 0.2	2.1 ± 1.2	−35 ± 4
U(VI)	$H_2DEH[MDP]$	−33.1 ± 0.5	−28.8 ± 0.7	14 ± 3
	$H_2DEH[EDP]$	−42.9 ± 0.6	−28.8 ± 0.5	47 ± 3
	$H_2DEH[BuDP]$	−29.5 ± 0.3	−16.3 ± 0.3	44 ± 2

term is observed for Am(III) extraction by H_2DEH[1,2-BzDP] and H_2DEH[MDP]. Am(III) can form highly stable 6- and 7-membered chelate rings with these ligands. The extraction of Am(III) by H_2DEH[1,2-BzDP], unlike H_2DEH[MDP] and the other alkylenedisposhonic acids, is not facilitated by a favorable entropic term, as typically observed for the formation of chelate complexes.[28] This result suggests no overall change in ordering of the system when Am(III) is extracted by H_2DEH[1,2-BzDP]. The almost zero or positive enthalpy change with an attendant favorable entropy change confirm, for H_2DEH[EDP] and for H_2DEH[BuDP], a micellar-like type of Am(III) extraction process.[13,25,29]

The extraction of Sr(II) by H_2DEH[1,2-BzDP] and H_2DEH[MDP] is enthalpy driven. However, H_2DEH[1,2-BzDP] complexes Sr(II) more strongly. With H_2DEH[EDP] and H_2DEH[BuDP], Sr(II) extraction is very inefficient, as indicated by the positive values of ΔG^0, as a result of strongly unfavorable entropy changes. The H_2DEH[EDP] results are indicative of strong metal–ligand coordination and attendant increased ordering in the organic phase. The negative entropy changes observed for the extractants also suggest that the ordering caused by hydration of the exchanged protons predominates over the dehydration of the metal ion in the aqueous phase. The observed entropy changes with H_2DEH[EDP] and H_2DEH[BuDP], and enthalpy changes with H_2DEH[EDP], do not suggest a micellar-type extraction mechanism for Sr(II), as was the case with Am(III).

The extraction of U(VI) by all three extractants is strongly driven by both favorable enthalpy and entropy variations, which testifies to the extremely high affinity exhibited, especially by H_2DEH[MDP] and H_2DEH[EDP], for U(VI), even in moderately high aqueous phase acid concentrations. The negative enthalpy change associated with metal coordination predominates over the other opposing enthalpic factors (metal ion dehydration, etc.). The favorable enthalpic changes observed for the extraction of U(VI) by H_2DEH[EDP] and H_2DEH[BuDP] do not suggest the weak bonding reminiscent of a micellar extraction mechanism as observed with Am(III) but, rather, the formation of highly stable complexes as with H_2DEH[MDP]. However, the larger entropy changes associated with H_2DEH[EDP] and H_2DEH[BuDP] in comparison to H_2DEH[MDP] suggest that a micellar extraction mechanism may be operative with these two extractants along with strong bonding.

The increasing ΔS^0 values observed for U(VI) extraction along the series H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP], may be due, to some degree, to the overlapping of a solvation mechanism with the ion exchange mechanism.[14] Extraction of uranyl nitrate by alkylphosphoric acids as solvated complexes at relatively high aqueous acidities is well known,[30] and was reported for alkylenediphosphonic acids as well.[6,9,10] 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 that have more basic P═O group, as observed along the H_2DEH[MDP], H_2DEH[EDP], H_2DEH[BuDP] series,[31] and would help in explaining, at least in part, the ΔS^0 trend reported for U(VI) in Table 3.

CONCLUSION

Thermodynamic parameters for the extraction of Am(III) and Sr(II) from aqueous HNO_3 solutions by *o*-xylene solutions of a new diphosphonic acid extractant, P,P′-di(2-ethylhexyl) benzene-1,2-diphosphonic acid (H_2DEH[1,2-BzDP]) were measured in the 25.0 to 60.0°C temperature range. The fact that the aggregation state of this extractant and the acid and extractant dependencies did not change with temperature allowed for the use of the temperature coefficient method to obtain the thermodynamic equilibrium constants and enthalpy changes for the metal distribution. The previously determined thermodynamic parameters with H_2DEH[MDP], H_2DEH[EDP], and H_2DEH[BuDP] were compared to those of this new extractant.

The extraction of Am(III) and Sr(II) by H_2DEH[1,2-BzDP] is strongly driven by enthalpy changes associated with the extraction process. Am(III) is extracted with essentially no change in ordering of the system, whereas the entropy change for the extraction of Sr(II) implies increased ordering, indicating that the hydration of the exchanged protons predominates over the dehydration of the aqueous phase metal ion.

The extractability of Am(III) follows the order H_2DEH[1,2-BzDP] > H_2DEH[MDP] > H_2DEH[EDP] > H_2DEH[BuDP]. The order of extraction of Sr(II) is H_2DEH[MDP] ≅ H_2DEH$[1,2-\mathrm{BzDP}]$ > H_2DEH [EDP] > H_2DEH[BuDP]. As anticipated, H_2DEH[1,2-BzDP] behaves more similarly to H_2DEH[MDP] than to H_2DEH[EDP]. This seems to indicate that the ligand preorganization introduced in the H_2DEH[1,2-BzDP] molecule by the rigid benzene ring has a stronger positive effect on the stability of the metal complexes than the negative effect due to an increase of the number of carbon atoms separating the two phosphorus atoms.

ACKNOWLEDGMENTS

This work was funded by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under contract number W-31-109-ENG-38. We thank P.G. Rickert of ANL for the preparation and purification of the extractants and K.L. Nash for helpful discussions.

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