

For submission to:

ANL/CHM-CP-103769

International Solvent Extraction Conference ISEC 2002

Cape Town, South Africa, March 18-21, 2002

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

Emmanuel O. Otu and Renato Chiarizia\*

Department of Chemistry, Indiana University Southeast, New Albany, IN 47150, USA

\*Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

The thermodynamics of extraction of Am(III), Sr(II) and U(VI) from aqueous HNO<sub>3</sub> solutions by *o*-xylene solutions of P,P'-di(2-ethylhexyl) methylene- (H<sub>2</sub>DEH[MDP]), ethylene- (H<sub>2</sub>DEH[EDP]), and butylene- (H<sub>2</sub>DEH[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 H<sub>2</sub>DEH[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 H<sub>2</sub>DEH[MDP] is enthalpy driven. The extraction of Am(III) by H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP] is mainly driven by entropy changes. The extraction of Sr(II) by H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP] is characterized by an unfavorable entropy change and is not indicative of a micellar-type extraction mechanism.

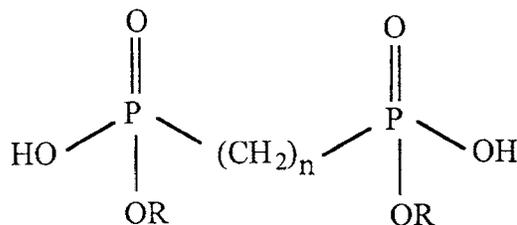
### INTRODUCTION

P,P'-di(2-ethylhexyl) alkylendiphosphonic 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- (H<sub>2</sub>DEH[MDP]), ethylene- (H<sub>2</sub>DEH[EDP]), and butylene- (H<sub>2</sub>DEH[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 H<sub>2</sub>DEH[MDP] exists as dimers [6], H<sub>2</sub>DEH[EDP] as hexamers [7], while H<sub>2</sub>DEH[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 H<sub>2</sub>DEH[MDP] or H<sub>2</sub>DEH[BuDP]. However, with H<sub>2</sub>DEH[EDP], extractant dependencies equal to unity were reported for these ions

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

indicating that, with H<sub>2</sub>DEH[EDP], extraction probably takes place through a micellar-type mechanism similar to other highly aggregated extraction systems [8-10].



Structure I

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 H<sub>2</sub>DEH[MDP], H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP] should be accompanied by different enthalpic and entropic contributions to the overall stability of the species formed.

## EXPERIMENTAL

<sup>241</sup>Am and <sup>233</sup>U were obtained from ANL stocks. <sup>85</sup>Sr 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., H<sub>2</sub>DEH[MDP] is dimeric, H<sub>2</sub>DEH[EDP] is hexameric, and H<sub>2</sub>DEH[BuDP] is predominantly trimeric in toluene [5-7]. The details of the VPO results and data treatment are reported elsewhere [11].

### Extraction Equilibria

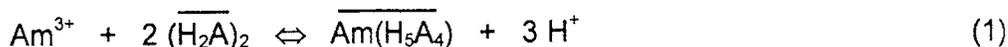
The extraction stoichiometries of the target ions by the extractants at ambient temperature have previously been determined [3-5]. Although the extractant aggregation did not change in the 25 to 60 °C temperature range, it was necessary to redetermine the extraction stoichiometries at various temperatures. 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 reagents 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

Ion	H <sub>2</sub> DEH[MDP]	H <sub>2</sub> DEH[EDP]	H <sub>2</sub> DEH[BuDP] trimer
Am(III)	2.0	1.0	1.5
Sr(II)	2.0	1.0	2.0
U(VI)	1.0	1.0	1.0

The extraction equilibrium of americium by the dimeric H<sub>2</sub>DEH[MDP] can be written as:



where H<sub>2</sub>A 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)-H<sub>2</sub>DEH[MDP] system can be written as:

$$K_{\text{Am,MDP}} = 4D \frac{[\text{H}^+]^3 \gamma_{\pm,\text{HN}}^6}{C_{\text{H}_2\text{A}}^2 \gamma_{\pm,\text{AmN}}^4} \quad (2)$$

where D is the molal distribution ratio,  $\gamma_{\pm,\text{HN}}$  and  $\gamma_{\pm,\text{AmN}}$  are the mean ionic molal activity coefficients of HNO<sub>3</sub> and Am(NO<sub>3</sub>)<sub>3</sub>, respectively, and C<sub>H<sub>2</sub>A</sub> is the molal analytical concentration of the extractant. Corresponding extraction equilibria and equilibrium constant expressions can also be written for the hexameric H<sub>2</sub>DEH[EDP] and the trimeric H<sub>2</sub>DEH[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 HNO<sub>3</sub> 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 H<sub>2</sub>DEH[MDP], H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP] in o-xylene.

T °C	logK Am(III)			logK Sr(II)			logK U(VI)		
	MDP	EDP	BuDP	MDP	EDP	BuDP	MDP	EDP	BuDP
25	8.82	4.67	1.49	1.80	-1.17	-2.21	5.63	7.31	5.06
30	8.78	4.66	1.50	1.78	-1.22	-2.16	5.54	7.23	5.01
35	8.75	4.68	1.54	-	-	-	5.54	7.14	4.96
40	8.71	4.66	1.54	1.70	-1.32	-2.17	5.38	7.07	4.92
45	8.68	4.66	1.58	1.67	-1.38	-2.19	5.32	7.00	4.88
50	8.65	4.66	1.59	1.64	-1.42	-2.16	5.22	6.93	4.83
60	8.59	4.64	1.67	1.58	-1.50	-2.15	5.10	6.78	4.76

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 H<sub>2</sub>DEH[MDP] has the highest extraction efficiency for the three metal ions (except for U(VI)) and H<sub>2</sub>DEH[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 ( $= -\Delta H^0/2.303R$ ) and intercepts ( $= \Delta S^0/2.303R$ ), respectively, of the plots of logK vs.  $1/T$ , with  $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ . Previously discussed conditions regarding the constancy of  $\Delta H^0$  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.

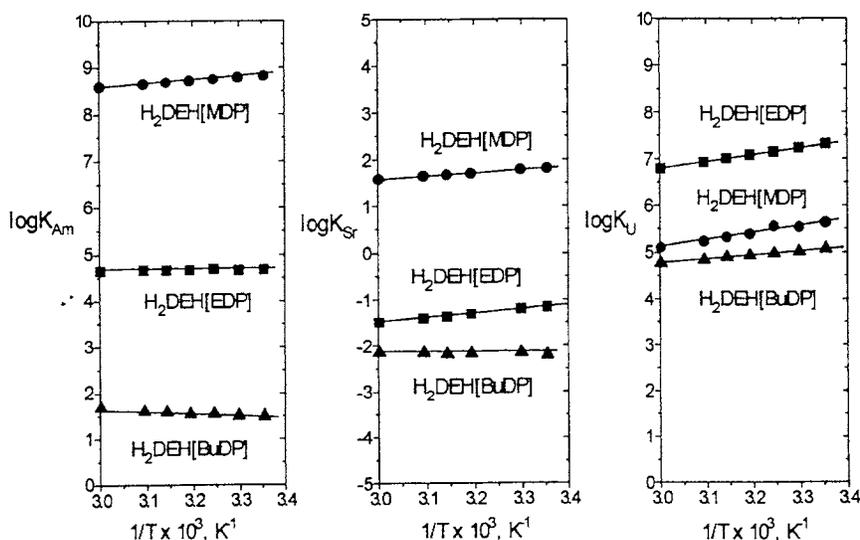


Figure 1. Effect of temperature on the extraction of Am(III), Sr(II) and U(VI) from aqueous HNO<sub>3</sub> by H<sub>2</sub>DEH[MDP], H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP] in *o*-xylene.

The  $\Delta H^0$  and  $\Delta S^0$  values calculated from the plots, along with the  $\Delta G^0$  values calculated from  $\Delta G^0 = -2.303RT\log K$  are given in Table 3. The uncertainties reported for  $\Delta H^0$  and  $\Delta S^0$  are the standard errors of the slopes and intercepts, respectively. Those for  $\Delta G^0$  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 ( $\Delta H > 0$ ) 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. 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 ( $\Delta H < 0$ ), as a consequence of replacing relatively weak hydrogen bonds 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 will produce opposite effects.

Table 3: Thermodynamic parameters for the extraction of Am(III), Sr(II) and U(VI) by H<sub>2</sub>DEH[MDP], H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP] in *o*-xylene.

Ion	Extractant	$\Delta G^{\circ}$ at 25 °C kJ/mol	$\Delta H^{\circ}$ kJ/mol	$\Delta S^{\circ}$ at 25 °C J/mol/K
Am(III)	H <sub>2</sub> DEH[MDP]	-50.3 ± 0.1	-12.5 ± 0.2	127 ± 1
	H <sub>2</sub> DEH[EDP]	-26.7 ± 0.5	-1.4 ± 0.5	85 ± 2
	H <sub>2</sub> DEH[BuDP]	-8.5 ± 0.7	9.5 ± 0.9	60 ± 4
Sr(II)	H <sub>2</sub> DEH[MDP]	-10.3 ± 0.1	-12.3 ± 0.4	-7 ± 1
	H <sub>2</sub> DEH[EDP]	6.7 ± 0.3	-18.2 ± 0.4	-84 ± 2
	H <sub>2</sub> DEH[BuDP]	12.6 ± 0.2	2 ± 1	-35 ± 4
U(VI)	H <sub>2</sub> DEH[MDP]	-32.2 ± 0.5	-30 ± 2	8 ± 2
	H <sub>2</sub> DEH[EDP]	-41.7 ± 0.6	-29 ± 1	44 ± 3
	H <sub>2</sub> DEH[BuDP]	-28.9 ± 0.3	-16 ± 1	42 ± 2

Among the ions investigated, Am(III) behaves in a way which is easier to rationalize based on the arguments outlined above. The  $\Delta H^{\circ}$  values for Am(III) extraction exhibit a trend along the H<sub>2</sub>DEH[MDP], H<sub>2</sub>DEH[EDP], H<sub>2</sub>DEH[BuDP] series, with the reaction being exothermic for the first, thermoneutral for the second, and endothermic for the third extractant, respectively. The trend in  $\Delta H^{\circ}$  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 H<sub>2</sub>DEH[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 H<sub>2</sub>DEH[EDP] and for H<sub>2</sub>DEH[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 H<sub>2</sub>DEH[MDP] is enthalpy driven. With H<sub>2</sub>DEH[EDP] and H<sub>2</sub>DEH[BuDP], Sr(II) extraction is very inefficient, as indicated by the positive values of  $\Delta G^{\circ}$ , as a result of strongly unfavorable entropic terms. The H<sub>2</sub>DEH[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 H<sub>2</sub>DEH[MDP] and H<sub>2</sub>DEH[EDP] for U(VI). The negative enthalpy change associated with metal coordination predominates over the other opposing enthalpic factors. The increasing  $\Delta S^{\circ}$  values observed for U(VI) extraction in moving from H<sub>2</sub>DEH[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 alkylendiphosphonic 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 H<sub>2</sub>DEH[MDP], H<sub>2</sub>DEH[EDP], H<sub>2</sub>DEH[BuDP] series (21), and would therefore explain the  $\Delta S^{\circ}$  trend reported for U(VI) in Table 2.

### 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

### REFERENCES

1. E.P. Horwitz, R. Chiarizia and M.L. Dietz (1997), *US Pat.*, No.5,651,883 (July 29).
2. R. Chiarizia, E. P. Horwitz, S. D. Alexandratos, and M. J. Gula (1997), *Sep. Sci. Technol.*, **32**, 1-35.
3. R. Chiarizia, E. P. Horwitz, P. G. Rickert and A. W. Herlinger (1996), *Solv. Extr. Ion Exch.*, **14**, 773-792.
4. R. Chiarizia, A. W. Herlinger and E. P. Horwitz (1997), *Solv. Extr. Ion Exch.*, **15**, 417-432.
5. R. Chiarizia, A. W. Herlinger, Y. D. Cheng, J. R. Ferraro, P. G. Rickert and E. P. Horwitz (1998), *Solv. Extr. Ion Exch.*, **16**, 505-526.
6. A. W. Herlinger, J. R. Ferraro, R. Chiarizia and E. P. Horwitz (1997), *Polyhedron* **16**, 1843-1854.
7. A. W. Herlinger, R. Chiarizia, J. R. Ferraro, P. G. Rickert and E. P. Horwitz (1997), *Solv. Extr. Ion Exch.*, **15**, 401-416
8. B. A. Moyer, C. F. Baes, Jr., G. N. Case, G. J. Lumetta and N. M. Wilson (1993), *Sep. Sci. Technol.*, **28**, 81-113.
9. G. S. Rao, G. W. Mason and D. F. Peppard (1966), *J. Inorg. Nucl. Chem.*, **28**, 887-897.
10. R. Chiarizia, R. C. Gatrone and E. P. Horwitz (1995), *Solv. Extr. Ion Exch.*, **13**, 615-645.
11. E. O. Otu and R. Chiarizia (2001), *Solv. Extr. Ion Exch.*, **19**, in press.
12. S. Kotrly and L. Sucha (1985), *Handbook of Chemical Equilibria in Analytical Chemistry*, J. Wiley & Sons, New York, pp. 116-117.
13. C. L. Kusik and H. P. Meissner (1978), *Electrolyte Activity Coefficients in Inorganic Processing*, in *Fundamental aspects of Hydrometallurgical Processes*, AIChE Symposium Series **173**, pp. 14-20.
14. E. O. Otu and R. Chiarizia (2001), *Solv. Extr. Ion Exch.*, submitted.
15. E. O. Otu and A. D. Westland (1990), *Solv. Extr. Ion Exch.*, **8**, 827-842.
16. E. O. Otu (1998), *Solv. Extr. Ion Exch.*, **16**, 1161-1176.
17. E. O. Otu (1999), *Thermochimica Acta*, **329**, 117-121.
18. G. R. Choppin and A. Morgenstern (2000), *Solv. Extr. Ion Exch.*, **18**, 1029-1049.
19. P.R. Danesi, R. Chiarizia, M.A. Raieh and G. Scibona (1975), *J. Inorg. Nucl. Chem.*, **37**, 1489-1493.
20. Y. Marcus and S. Kertes (1969), *Extraction by Compound Formation*, in *Ion Exchange and Solvent Extraction of Metal Complexes*, J. Wiley & Sons, New York, p. 545.
21. D. R. McAlister, M. L. Dietz, R. Chiarizia, P. R. Zalupski and A. W. Herlinger (2001) *Sep. Sci. Technol.*, in press.