J. inorg. nucl. Chem., 1970, Vol. 32, pp. 1011 to 1022. Pergamon Press. Printed in Great Britain

PARTITION OF OXIDIZED AMERICIUM FROM ACTINIDES(III) AND LANTHANIDES(III)*

G. W. MASON, A. F. BOLLMEIER and D. F. PEPPARD
Chemistry Division, Argonne National Laboratory, Argonne, Ill. 60439

(*Received* 18 *August* 1969)

Abstract—In the liquid–liquid extraction system 0·6 F bis (2,6-dimethyl-4-heptyl) phosphoric acid, $(C_9H_{19}O)_2PO(OH)$, HD(DIBM)P, in *n*-heptane vs. an aqueous 0·025 F HNO_3 + 0·025 F $AgNO_3$ + 0·185 F $K_2S_2O_8$ phase the *K* for oxidized Am, presumably Am(VI), is greater than 40 while that for Cm(III) is less than 1×10^{-5}. Correspondingly, the *K* values for each M(III) actinide and lanthanide tested is less than 1×10^{-3}. Consequently, this system may be used for the purification of americium with respect to M(III) actinides and lanthanides or alternatively for the purification of M(III) actinides and lanthanides with respect to americium. Details of the mutual separation of ^{241}Am and ^{244}Cm through the application of this liquid–liquid extraction system are given. Proposed extension of the study to extraction chromatography employing HD(DIBM)P as the stationary phase is discussed.

IN A STUDY, to be reported later, of the effect of the nature of X and Y upon the extractive power of (X)(Y)PO(OH) for M(III) and M(IV) lanthanides and actinides and M(VI) actinides, it was found that bis(2,6-dimethyl-4-heptyl) phosphoric acid, HD(DIBM)P, discriminates strongly in favor of U(VI) with respect to all M(III) lanthanides and actinides. The highly favorable M(VI) to M(III) discrimination suggested the applicability of HD(DIBM)P to the separation of americium as Am(VI) from all actinides(III) and lanthanides(III). A system embodying HD(DIBM)P in a saturated hydrocarbon carrier diluent vs an aqueous HNO_3 plus oxidant phase applicable to the purification of americium with respect to lanthanides(III) and actinides(III) and/or purification of any of these M(III) elements, including Cm(III), with respect to americium is described.

EXPERIMENTAL

The extractant, HD(DIBM)P, bis(2,6-dimethyl-4-heptyl) phosphoric acid, $[(i\text{-}C_4H_9)_2CHO]_2PO(OH)$, was prepared and purified by procedures adapted from those reported for other $(GO)_2PO(OH)$ extractants[1, 2]. The alcohol used in its preparation, 2,6-dimethyl-4-heptanol, also called di-isobutyl carbinol, was obtained as a 99·9 per cent purity product from Union Carbide Corporation, Chemicals Division.

A commercial grade of dinonyl phosphate in which the nonyl group was 2,6-dimethyl-4-heptyl, was formerly available from Oldbury Electrochemical Company. All attempts to isolate pure HD(DIBM)P from this material led to a product (no di-acidic component detected) whose equivalent weight was low.

After high purity 2,6-dimethyl-4-heptanol became available, synthesis of pure HD(DIBM)P was attempted. The equivalent weight of the initial preparations in which the reaction mixture was refluxed was low by 3–5 per cent, although there was no detectable di-acidic contaminant.

But when the reaction temperature was kept below 15°C a mixture was obtained from which pure HD(DIBM)P was isolated in yields of 60–70 per cent based upon the quantity of $POCl_3$ used.

---

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

1. D. F. Peppard, G. W. Mason and C. M. Andrejasich, *J. inorg. nucl. Chem.* **27**, 697 (1965).
2. D. F. Peppard, G. W. Mason and G. Giffin, *J. inorg. nucl. Chem.* **27**, 1683 (1965).

A typical example of the preparation and purification of HD(DIBM)P is described in detail.

A 3-l round bottom 3-neck flask equipped with a stirrer, thermometer and adding funnel continuously flushed with a slow stream of dry nitrogen and immersed in a cooling bath is used as the reaction vessel. To a solution of 721 g (5·0 moles) of 2,6-dimethyl-4-heptanol, 395 g (5·0 moles) of pyridine, and 1 l. of benzene in the reaction vessel, 306 g (2·0 moles) of $POCl_3$ is added dropwise from the adding funnel over a period of 3 hr. During this period the reaction mixture is stirred and kept at 10–15°C.

After the addition of $POCl_3$ is complete, stirring is continued for 2 hr allowing the mixture to warm to room temperature. The reaction mixture is then allowed to stand without stirring for approximately 16 hr (overnight).

The mixture is stirred with 1 l. of 2 M HCl for 5 min. The resultant liquid mixture is transferred to a 5-l separatory funnel for separation of phases. The lower phase (aqueous) is discarded. The upper phase is scrubbed successively with two 1-l. portions of 1 M HCl with 3-min stirring times. The lower (aqueous) phase is discarded.

The scrubbed mixture is transferred to a 3-l beaker and stirred (magnetically on a hot plate) with 500 ml of 3 M HCl at about 90°C for 3 hr. (The benzene evaporates during this operation.) The primary purpose of this step is to complete the destruction of all P–Cl bonds. Simultaneously, most of the P–O–P bonds are destroyed.

Again, the mixture is transferred to a separatory funnel for the removal and discard of the lower (aqueous) phase.

The mixture is then transferred to a 2-l. round bottom flask. Alcohol and water are removed at approximately 0·05 mm, using magnetic stirring, as the surrounding water bath is slowly brought from room temperature to 60°C.

The magnetically-stirred product is then heated under reflux with 500 ml of 3 M HCl for 48 hr to complete the destruction of P–O–P bonds.

The mixture of aqueous phase and viscous organic phase is again transferred to the 5-l. separatory funnel. A 2·5-l. portion of *n*-heptane to be added is used to rinse the adhering viscous product from the flask into the funnel. After the phases are mixed for 3 min the separated aqueous phase is discarded.

The organic phase is then scrubbed successively with nine 500-ml portions of ethylene glycol using 3-min contact times. The lower (ethylene glycol) phases may be set aside for recovery of mono 2,6-dimethyl-4-heptyl phosphoric acid, $(C_9H_{19}O)PO(OH)_2$.

Following three successive scrubs with 1-l. portions of distilled water (3-min contact times), the scrubbed organic phase is transferred to a 3-l. beaker. The *n*-heptane is removed (without heating) by blowing air across the open beaker.

Finally, the product is transferred to a 2-l. round bottom flask and volatile components removed (magnetic stirring) without heating at approximately 0·05 mm. To ensure complete removal of traces of alcohol, stirring at 0·05 mm is continued for a total of 16 hr.

The yield of this final product, based upon the quantity of $POCl_3$ used, was 65 per cent in a specific preparation.

This specific product was analyzed for C, H and P by Schwarzkopf Microanalytical Laboratory, and titrated as described previously[1] to determine its equivalent weight. No diacidic component was detected.

Anal. Calcd. for $(C_9H_{19}O)_2PO(OH)$: C, 61·68; H, 11·22; P, 8·84. Equivalent Weight (350·5 g). Found: C, 60·57; H, 11·16; P, 8·07. Equivalent Weight (354 g).

It was then titrated in 75% ethanol, as described previously[1] and the p*K* in 75% ethanol at 22 ± 2°C was calculated to be 4·75. From isothermal distillation data obtained with a Thomas Isothermal Molecular Weight Apparatus the compound was shown to be dimeric in *n*-heptane at 30·4°C.

Since the extractant, HD(DIBM)P, is dimeric in dry *n*-heptane but of undetermined molecular complexity in the system under study, ambiguity is avoided through the use of the concentration unit, formality, F, defined here as the number of formula weights of solute per liter of solution.

Argonne National Laboratory stock samples of 470-yr^{241}Am and 18-yr^{244}Cm were purified by liquid–liquid extraction in the system 0·60 F HD(DIBM)P in *n*-heptane vs. an aqueous 0·025 F $HNO_3 + 0{\cdot}025$ F $AgNO_3 + 0{\cdot}185$ F $K_2S_2O_8$ phase. The beta active lanthanide tracers were obtained as described previously[3].

---

3. D. F. Peppard, G. W. Mason and S. Lewey, *J. inorg. nucl. Chem.* **27**, 2065 (1965).

The *n*-heptane used as diluent was the Phillips Petroleum Company "pure grade". In preparing it for use, 600 ml was heated with 5 g of bromine at 60°C for 2 hr. After cooling to room temperature it was scrubbed with two 600 ml portions of distilled water.

This pretreated *n*-heptane was used in preparing solutions of HD(DIBM)P. Each HD(DIBM)P solution was then pretreated, shortly before use, by shaking it with an equal volume of a saturated aqueous solution of $K_2S_2O_8$, 0·05 F in $AgNO_3$, at 70°C for 1 hr.

All equipment which would come in contact with either or both of these phases was also pretreated by heating it in contact with a saturated aqueous solution of $K_2S_2O_8$, 0·05 in $AgNO_3$ and 0·05 in HNO_3, at 70°C for 1 hr.

In the determination of the distribution ratio, K, for a given element that element was added as an alpha-active or beta-active nuclide to a 2-ml portion of the pertinent aqueous phase. The solution was heated at 50°C for 10 min, then added to a 2-ml portion of the pertinent pretreated extractant phase in a stoppered 5-ml graduated cylinder initially at room temperature (22+2°C). Following a 3 min period of manual shaking the phases were separated and transferred separately to centrifuge cones. After centrifugation to assure clarification of phases each phase was assayed for its alpha-active or beta-active component as described previously[4]. A suitable aliquot of the organic phase was prepared for radiometric assay by evaporation on a 3-ml platinum disc. But since the aqueous phase had a high salt content the radioactive nuclide was extracted from it into a 1 per cent solution of "di-octyl pyrophosphate" as described previously[4], and a suitable aliquot of the extract was evaporated on a 3-ml platinum disc. The ratio of the counting rates associated with equal aliquots of the two phases is reported as the distribution ratio, K, the counting rate of the organic phase being the numerator and that of the aqueous phase the denominator.

All K values of Tables 1 and 3 were obtained in this way, and the individual contacts in the separations represented by the data of Table 2 were performed similarly. But in the systems of Table 2, ^{241}Am and ^{244}Cm were simultaneously present in the aqueous phase used as feed.

In Experiment 1, Table 2, a 2-ml portion of feed was contacted with a 2-ml portion of organic extractant phase for 3 min. The separated organic phase was then contacted with a 2-ml portion of barren aqueous scrub (0·025 F HNO_3 + 0·025 F $AgNO_3$ + 0·185 F $K_2S_2O_8$, heated at 50°C for 10 min just preceding use) for 3 min. The aqueous phases were discarded since the purpose was to demonstrate a clean-up of ^{241}Am, the minor component of the feed material (in terms of radioactivity counting rate). The Am/Cm ratio was raised from $9{\cdot}2 \times 10^{-3}$ in the feed to $9{\cdot}7 \times 10^2$ in the product. Considering the decontamination factor D.F., to be defined as a quotient: the (Am/Cm) ratio in the product divided by the (Am/Cm) ratio in the feed, the D.F. exceeds $1{\cdot}1 \times 10^5$.

In Experiment 2, Table 2, a 2-ml portion of feed was contacted successively with four 2-ml portions of organic extractant phase, the first contact time being 3 min and the last three being 2 min. (The aqueous phase was heated at 50°C for 10 min preceding the first contact but not between contacts.) The organic phases were discarded since the purpose was to demonstrate a clean-up of ^{244}Cm, the minor component of the feed material (in terms of radioactivity counting rate). The Cm/Am ratio was raised from 0·016 in the feed to 25 in the product. The D.F. was $1{\cdot}6 \times 10^3$.

In Experiment 3, Table 2, a 2-ml portion of feed was contacted successively with four 2-ml portions of organic extractant phase and it was followed by a 2-ml portion of barren aqueous phase (scrub, identical with the feed makeup except that it contained no Am or Cm). All contact times were 5 min. (Note that both the feed and the scrub were heated at 50°C for 10 min before initial use.) The four organic phases were combined and assayed as Am product. The two aqueous phases were combined and assayed as Cm product. The Am/Cm ratio was raised from 0·61 in the feed to $7{\cdot}1 \times 10^2$ in the Am product, the D.F. being $1{\cdot}2 \times 10^3$. The Cm/Am ratio was raised from 1·6 in the feed to $>4{\cdot}2 \times 10^2$ in the Cm product, the D.F. being $>2{\cdot}6 \times 10^2$.

In each of the separations reported in Table 2, the content of contaminant nuclide in the product nuclide was determined by alpha pulse analysis employing a silicon surface barrier detector fabricated at Argonne National Laboratory, an Instrument and Development Products amplifier and a Nuclear Data 180 512-channel analyzer.

Since all transfers were made by pipet, sizable losses of product were inevitably incurred in ensuring the absence of one phase in the other. It is evident that yields should properly be calculated in terms of losses to the opposing product, since on an operational basis the above losses would not be

---

4. D. F. Peppard, G. W. Mason and I. Hucher, *J. inorg. nucl. Chem.* **18**, 245 (1961).

Table 1. Operational dependence of the *K* for Am and Cm upon the concentration of HD(DIBM)P and of HNO_3 in the system HD(DIBM)P in *n*-heptane vs. an aqueous $HNO_3 + 0{\cdot}025$ F $AgNO_3 + 0{\cdot}185$ F $K_2S_2O_8$ phase*

	Initial conditions		*K*	
Set	F HD(DIBM)P	F HNO_3	Am	Cm
A	0·075	0·025	4·9	$<6\times10^{-6}$
A	0·15	0·025	7·7	$<6\times10^{-6}$
A	0·30	0·025	16·9	$<6\times10^{-6}$
A	0·60	0·025	44·9†	6×10^{-6}‡
B	0·60	0·025	49·2†	6×10^{-6}
B	0·60	0·05	30·0	$<6\times10^{-6}$
B	0·60	0·10	16·3	$<6\times10^{-6}$
B	0·60	0·20	6·2	$<6\times10^{-6}$

*In each case a 2-ml portion of the aqueous phase containing ^{241}Am or ^{244}Cm was heated at 50°C for 10 min, then transferred without cooling to a 5-ml graduated cylinder containing 2-ml of the barren organic phase (at 22 ± 2°C). The mixture was immediately shaken manually for 3 min. The separated phases were then assayed for Am or Cm.

†Within experimental error *K* for Am remains unchanged from that in the system 0·60 F HD(DIBM)P in *n*-heptane vs. an aqueous 0·025 F $HNO_3 + 0{\cdot}025$ F $AgNO_3 + 0{\cdot}185$ F $K_2S_2O_8$ phase when either the $AgNO_3$ or the $K_2S_2O_8$ concentration is decreased by three successive factors of two, but with decreasing concentration of $S_2O_8^{-2}$ the *K* for Cm increases (cf. Table 3).

‡In this system, the *K* values for Pm, Eu, Tm and Y are all less than 1×10^{-3}. The *K* for Cm in the system 0·6 F HD(DIBM)P in *n*-heptane vs. 0·025 F HNO_3 (no Ag^+ or $S_2O_8^{-2}$ present) is 2×10^{-2}.

experienced. In this light, the product yield in each of the experiments of Table 2 may be considered nearly quantitative, in each case well over 99 per cent.

In the system 0·6 F HD(DIBM)P in *n*-heptane vs. aqueous 0·025 M HNO_3 the *K* for Am(III) is less than 2×10^{-2}, so it is apparent that extracted Am may be returned to an aqueous HNO_3 phase readily if it is first reduced to Am(III). A convenient procedure consists of contacting the organic extract of Am with an equal volume of 1·0 M HNO_3 containing approximately 2% hydrogen peroxide for 3 min. Less than 0·01 per cent of the Am remains in the organic phase. The return may equally well be effected through use of HCl or H_2SO_4 in place of HNO_3.

Since the trace of HD(DIBM)P held mechanically and/or in true solution by the aqueous Am or Cm product phase may interfere in further processing or measurements it should be removed. This removal is readily accomplished by contacting the aqueous product phase successively with three equal-volume portions of *n*-decyl alcohol or 2-ethyl hexyl alcohol. Traces of the alcohol are then removed by contacting the aqueous product phase successively with two equal-volume portions of *n*-heptane.

RESULTS AND CONCLUSIONS

From Table 1, the *K* for oxidized Am is seen to increase with increasing concentration of extractant in the organic phase and with decreasing concentration of HNO_3 in the aqueous phase, the variation being approximately linear. At

Table 2. Mutual separation of ^{241}Am and ^{244}Cm in the system 0·6 F HD(DIBM)P in *n*-heptane vs. an aqueous 0·025 F HNO_3 + 0·025 F $AgNO_3$ + 0·185 F $K_2S_2O_8$ phase

	Feed (Aq.)		Am prod. (Org.)		Cm prod. (Aq.)		D.F.	
Expt. No.	(c/m)	(Am/Cm*)	(c/m)	(Am/Cm*)	(c/m)	(Cm/Am*)	(Am/Cm)	(Cm/Am)
1	$1{\cdot}0 \times 10^6$	$9{\cdot}2 \times 10^{-3}$	$8{\cdot}9 \times 10^3$	$>9{\cdot}7 \times 10^2$			$>1{\cdot}1 \times 10^5$	
2	$6{\cdot}3 \times 10^5$	62			$1{\cdot}1 \times 10^4$	25		$1{\cdot}6 \times 10^3$
3	$1{\cdot}6 \times 10^6$	0·61	$5{\cdot}3 \times 10^5$	$7{\cdot}1 \times 10^2$	$9{\cdot}9 \times 10^5$	$>4{\cdot}2 \times 10^2$	$1{\cdot}2 \times 10^3$	$>2{\cdot}6 \times 10^2$

Both organic and aqueous phases were used in 2-ml portions, a single portion of aqueous Feed, contacted with one or four portions of initially barren organic phase, being followed (in Experiments 1 and 3) by one portion of initially barren aqueous phase (scrub).

Immediately before initial contact each aqueous phase (including initially barren scrub) was heated at 50°C for 10 min.

Expt. 1: 1 org., 2 aq. phases. The minor component, Am, decontaminated from Cm.
Expt. 2: 4 org., 1 aq. phase. The minor component, Cm, decontaminated from Am.
Expt. 3: 4 org., 2 aq. phases. Am and Cm, initial ratio nearly unity, decontaminated mutually.

*All ratios are expressed in terms of alpha counting rates.

Table 3. *K* values for Cm(III) in the system HDEHP in *n*-heptane vs. aqueous HNO_3, with and without $K_2S_2O_8$

F HDEHP	F HNO_3	F $K_2S_2O_8$	*K*
0·30	0·025	0	$1·3 \times 10^3$
0·30	0·025	0·093*	1·6
0·30	0·10	0	11·8
0·30	0·10	0·093*	0·50
0·60	0·025	0	$6·0 \times 10^3$
0·60	0·025	0·048	$4·8 \times 10$
0·60	0·025	0·095	$1·0 \times 10$
0·60	0·025	0·19	1·8

*The aqueous phase contained 0·025 F $AgNO_3$.

concentrations of extractant appreciably greater than 0·6 F the phases did not disengage as quickly as under the conditions reported and at concentrations of HNO_3 appreciably less than 0·025 F it was difficult to obtain reproducible data. The *K* for Cm(III) is acceptably low in each of the experiments reported in Table 1. Accordingly the operating parameter values: 0·6 F extractant, 0·025 F HNO_3, 0·025 F $AgNO_3$ and 0·185 F $K_2S_2O_8$ were chosen for the separations reported in Table 2.

Under the experimental conditions of Table 2, the *K* for Cm(III) is 6×10^{-6}. In an identical system except that $AgNO_3$ and $K_2S_2O_8$ are absent the *K* for Cm(III) is 2×10^{-2}, Table 1, footnote. The depression of the *K* for Cm(III) by a factor of 3×10^3 by the "oxidizing solution" is presumably due primarily to complexing of Cm(III) by persulfate. Probably, the *K* for oxidized Am is also depressed through persulfate complexing.

In the separations experiments of Table 2, ratios are expressed in terms of measured alpha counting rates associated with the Am and Cm content of the sample, not in terms of masses of the two elements.

In Experiment 1, the initial mixture of the elements contained Am as the minor component, the ratio Am/Cm being $9·2 \times 10^{-3}$. The Am/Cm ratio in the product Am, obtained in a yield greater than 90 per cent (probably greater than 97 per cent), was greater than $9·7 \times 10^2$. The decontamination factor, D.F., was in excess of $1·1 \times 10^5$.

In Experiment 2, Cm was the minor component of the initial mixture, the Am/Cm ratio being 62, i.e. Cm/Am = 0·016. The Cm/Am ratio in the product Cm, obtained in essentially quantitative yield, was 25. The D.F. was $1·6 \times 10^3$.

In Experiment 3, the initial mixture contained comparable amounts of Am and Cm, the Am/Cm ratio being 0·61. Both product Am and product Cm were obtained. In the product Am (measured yield 87 per cent) the Am/Cm ratio was $7·1 \times 10^2$ indicating a D.F. of $1·2 \times 10^3$. In the product Cm(essentially quantitative yield, as measured), the Cm/Am ratio was greater than $4·2 \times 10^2$ indicating a D.F. greater than $2·6 \times 10^2$.

As pointed out under Experimental the yields, with respect to the chemistry involved, in each of the experiments reported in Table 2 must be in excess of

99 per cent since there are only two product phases, both liquid. The lower reported yields are due to mechanical losses incurred in transfers and in separations of phases as well as to difficulties associated with the measurements of small volumes. In larger scale liquid–liquid operations and in extraction chromatography these losses and apparent losses would not be incurred.

It is evident from the data of Table 2 that americium and curium may be mutually separated with essentially quantitative yield of each element. Presumably any desired D.F. may be realized through the use of multiple extractions and scrubs. From a separations viewpoint it is important to note that in the system presented in Table 2 (very strong oxidizing environment) cerium, uranium, neptunium, plutonium and berkelium are also preferentially extracted and accompany americium. However, cerium and berkelium are readily extracted from Am(III) in their tetravalent form in another system[5], and a wide variety of processes are available for purifying americium with respect to uranium, neptunium and plutonium.

From the *K* values reported for selected lanthanides(III), Table 1, footnote, it is clear than the lanthanide content of an americium product may be reduced to any desired level.

The depressant effect of the persulfate oxidant upon the *K* for Cm(III) is shown in Table 3. From the first four lines of data, the relative effect is seen to be greater at 0·025 F HNO_3 than at 0·10 F. The last four lines of data show the effect of varying the concentration of $K_2S_2O_8$. It is evident that complexing of Cm(III) by $S_2O_8^{-2}$ and/or $HS_2O_8^{-1}$ in these systems has lowered the concentration of unbound Cm(III) to a very small fraction of the total concentration of Cm(III) present in the aqueous phase.

DISCUSSION

The problem of the mutual separation of americium and curium is of great importance in nuclear science and engineering[6–9] and consequently has been investigated from a variety of approaches. The most attractive of these, on the basis of initial promise, have been based upon the observation that americium may be obtained in aqueous solution in a valence above +3[10] with curium retaining its trivalent state[10c]. For example, since U(VI) is known to extract with a *K* far higher than that of Am(III) or Cm(III) in a large number of liquid–

---

5. D. F. Peppard, S. W. Moline and G. W. Mason, *J. inorg. nucl. Chem.* **4**, 344 (1957).
6. R. D. Baybarz and R. E. Leuze, *Nucl. Sci. Engng* **11**, 90 (1961).
7. (a) W. D. Burch, E. D. Arnold and A. Chetham-Strode, *Nucl. Sci. Engng* **17**, 438 (1963); (b) R. E. Leuze, *Nucl. Sci. Engng* **17**, 448 (1963); (c) M. H. Lloyd, *Nucl. Sci. Engng* **17**, 452 (1963); (d) O. O. Yarbro, J. L. English and T. S. Mackey, *Nucl. Sci. Engng* **17**, 492 (1963).
8. D. E. Ferguson and J. E. Bigelow, *Actinides Rev.* **1**, 213 (1969).
9. *Californium-252*, Proceedings of a Symposium sponsored by The New York Metropolitan Section of the American Nuclear Society, New York City, October 22, 1968. Edited by James J. Barker, Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Virginia, 1969.
10. (a) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *J. Am. chem. Soc.* **72**, 1425 (1950); (b) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *J. Am. chem. Soc.* **73**, 5715 (1951); (c) S. E. Stephenou and R. A. Penneman, *J. Am. chem. Soc.* **74**, 3701 (1952); (d) M. Ward and G. A. Welch, *J. chem. Soc.* **1954**, 4038.

liquid extraction systems, it seemed logical that Am(VI) could be preferentially extracted with respect to Cm(III) in a suitable liquid–liquid extraction system.

Peppard and Mason[11] reported the extraction of Am(VI) from Cm(III) in the system 0·3 F HDEHP in *n*-heptane vs. 0·1 F HNO_3 plus 0·1 F $(NH_4)_2S_2O_8$, where HDEHP is bis 2-ethyl hexyl phosphoric acid, $(2\text{-}C_2H_5 \cdot C_6H_{12}O)_2PO(OH)$. (In the introductory paragraph of that report the diluent is incorrectly identified as toluene.)

The report in [11], under the names of D. F. Peppard and G. W. Mason, falls in the unusual category of inadvertent publication. Peppard and Mason had developed a sporadically successful Am(VI) vs. Cm(III) separation process based upon extraction of Am(VI) by HDEHP from dilute HNO_3 containing $(NH_4)_2S_2O_8$. Their notes were made available to a team of nuclear chemists faced with the problem of purifying a sample of Am with respect to Cm. The process proved successful in this application. Through a misunderstanding, the Peppard and Mason notes (unfortunately incorrectly transcribed) were interpreted as a contribution to The Radiochemistry of Americium and Curium, NAS-NS 3006, and were published as such. If two errors are corrected and one ambiguity removed, that report titled "Separation of Am from Cm by Solvent Extraction" represents the state of the art in the authors' laboratory in 1959. In the opening paragraph read *n*-heptane for toluene. Throughout read 0·2 M for 0·1 M in reference to $(NH_4)_2S_2O_8$. In step 3, read $\frac{1}{4}$ to $\frac{1}{3}$ for 1-4 to 1-3.

However, no such extraction system has been reported in which the americium behaves reproducibly unless it is present in relatively high concentration, perhaps 0·1 mg/ml[11].

Consequently, the mutual separation of americium and curium has to a major degree been accomplished through ion exchange or extraction chromatography techniques, in many instances utilizing a separation factor for the M(III) elements considerably below 2·0. The values of 2·7[12] and 3·0[13] reported recently are the highest yet realized for the separation factor for these elements in their trivalent states.

Of course, extraction chromatography involving Am(VI) takes advantage of far larger separation factors. For example Hulet[14] used HDEHP on a silica support and eluted with 0·10 F HNO_3. He obtained an Am fraction having a D.F. from Cm of 1000 and a Cm fraction having a D.F. from Am of 10–14, stating that: "Varying the oxidation conditions, stationary phase preparation, and eluate flow rates was ineffectual in reducing the incipient break-through of Am(III) into the Cm fraction." But he continued: "Nevertheless, improvements that would lead to the complete separation of Am and Cm are still believed likely."

The difficulty encountered in the HDEHP extraction of oxidized americium from an aqueous phase containing HNO_3 and persulfate ion is two-fold. In order to keep the K for Cm(III) below unity the concentration of HNO_3 must be kept reasonably high, the K for Cm(III) being approximately inversely third power dependent upon the H^+ concentration in the aqueous phase. But in the presence

---

11. D. F. Peppard and G. W. Mason, *The Radiochemistry of Americium and Curium*, Procedure 7, p. 34. Nat. Res. Council, Nucl. Sci. Ser. NAS-NS 3006 (1960).
12. (a). E. P. Horwitz, K. A. Orlandini and C. A. A. Bloomquist, *Inorg. nucl. chem. Lett.* **2**, 87 (1966). (b). E. P. Horwitz, C. A. A. Bloomquist, K. A. Orlandini and D. J. Henderson, *Radiochim. Acta* **8**, 127 (1967).
13. J. Van Ooyen, Solvent extraction chemistry, *Proc. Int. Conf. held at Gothenburg, Sweden*, p. 485. August 27–September 1, 1966. North-Holland, Amsterdam (1967).
14. E. K. Hulet, *J. inorg. nucl. Chem.* **26**, 1721 (1964).

of a high concentration of H^+ ion the persulfate system generates hydrogen peroxide[15] which reduces the americium[16]. So the oxidation of americium is accompanied by a competing reduction. Additionally, as the water is oxidized the acidity of the aqueous phase is increased. Consequently, the *K* for Am(VI) is decreased since it decreases with increasing hydrogen ion concentration in the aqueous phase. So, since in this system the ratio of the *K* for Am(VI) to that for Cm(III) is not large, it is difficult to maintain a hydrogen ion concentration such that the *K* for Am(VI) is greater than unity and that for Cm(III) is less than unity.

The difficulty of holding the *K* for Cm below unity is compounded by the depressant action of persulfate ion upon the *K* for Cm. See Table 3. Under the conditions specified[11] for the separation of Am from Cm, 0·3 F HDEHP in *n*-heptane vs. an aqueous 0·1 F HNO_3 + 0·2 M $(NH_4)_2S_2O_8$ phase, the *K* for Cm is slightly less than 10^{-1}. In a system identical to this except that $S_2O_8^{-2}$ is absent the *K* for Cm is approximately 12. (Table 3 illustrates the effect of increasing the concentration of persulfate ion.)

From these considerations it is concluded that a suitable liquid–liquid extraction system should: (1) Exhibit a high discrimination in favor of oxidized americium with respect to curium(III), (2) be operable at an acidity below that at which production of hydrogen peroxide by persulfate becomes significant. These criteria are met by the system 0·6 F HD(DIBM)P in *n*-heptane vs. aqueous 0·025 F HNO_3. Presumably because of steric factors HD(DIBM)P is a far poorer extractant for M(III) lanthanides and actinides than is HDEHP. For example, in the 0·6 F extractant in *n*-heptane vs. 0·025 F HNO_3 system the approximate *K* values for Cm(III) associated with the two extractant are: 6×10^3, HDEHP (Table 3); 2×10^{-2} HD(DIBM)P (Table 1, footnote). But the *K* values for U(VI) associated with the two extractants are both greater than 500.

Under the experimental conditions represented by Tables 1 and 2 no difficulty has been experienced in oxidizing ^{241}Am in low concentration to an extractable form. For example, in an experiment using the system represented in Table 2 and an aqueous phase initially containing less than 10^{-7} mg of ^{241}Am/ml (no ^{244}Cm) the *K* was 53.

Presumably, considering the oxidation conditions employed, the extracted americium is Am(VI)[10, 16]. However, the present study does not establish the oxidation state of the extracted element so the term "oxidized americium" is used. The *K* data of Table 1 represent only lower limits of the true *K* for oxidized americium since it is evident that the *K*, as measured, is limited by the extent to which the americium has been oxidized. For example, in experiments in which oxidized americium has been extracted into the 0·6 F HD(DIBM)P phase from 0·025 F HNO_3 + 0·025 F $AgNO_3$ + 0·185 F $K_2S_2O_8$ and the separated organic extract then contacted with a barren aqueous scrub of the foregoing composition, the *K* for the second contact has invariably been approximately twice that for the first. In one instance the two respective *K* values were 56 and 114. An attempt to measure the true *K* for the oxidized form of americium, probably Am(VI), is being made.

[15] I. M. Kolthoff and I. K. Miller, *J. Am. chem. Soc.* **73**, 3055 (1951).

[16] R. A. Pennemann and L. B. Asprey, *Proc. Int. Conf. peaceful Uses atom. Energy, Geneva*, Vol. 7, p. 355. United Nations (1956).

From the data of Table 2 it is apparent that this extraction system offers mutual separation of the two elements, americium and curium, to any desired degree of separation. Alternatively, it may be used to effect the purification of only one of the elements with respect to the other. Applicability of the system to the removal of lanthanides and/or other actinides from americium is evident. For example, some americium samples presently being studied were isolated by techniques employing carrying of the americium upon a precipitated lanthanum compound. In many cases the subsequent removal of lanthanum from the americium product was incomplete. This removal may be accomplished readily through extraction of oxidized americium by HD(DIBM)P from an aqueous HNO_3 solution, the lanthanum reporting predominately to the aqueous phase. Similarly, certain gross contaminant cations such as alkali and/or alkaline earths, and anions such as silicates, phosphates and fluorides may be removed from americium.

As noted in Results and Conclusions, cerium, uranium, neptunium, plutonium and berkelium are preferentially extracted along with oxidized americium. A study of the feasibility of returning americium as Am(III) to an aqueous phase while retaining some or all of the foregoing elements preferentially in the organic phase is in progress.

The system, as described, employs HNO_3 in the aqueous phase. It is equally effective if HNO_3 is replaced by H_2SO_4. But if H_2SO_4 is used the K for oxidized americium is somewhat lower, presumably because of aqueous phase complexing by the sulfate and/or bisulfate ion.

Although this separations system seems especially promising for adaptation to programs of large-scale isolation of pure americium and/or curium in nuclear processing plants it is applicable, also, to the problems encountered by the nuclear scientist working on the sub-micro microgram scale. The large D.F. (americium with respect to curium or vice versa) available in a single contact makes this an attractive system for use in experiments in which speed of operation is of prime importance.

For many applications, for example in small-scale nuclear studies in which remote control manipulations are required, it seems desirable to replace the extraction system described above by an extraction chromatography system derived from it. The first advantage of the chromatography technique over liquid–liquid extraction, greater ease of physical manipulation, is immediately apparent. But a second, elimination of losses through pipet transfers, and a third, elimination of unnecessary contamination of product through faulty phase separation, are also quite important. Hulet[14] has commented upon these advantages of extraction chromatography in isolating Bk.

Exploratory experiments have demonstrated the feasibility of adapting this system to extraction chromatography. No equilibration difficulties have been encountered with either ^{244}Cm or oxidized ^{241}Am. Destruction or inhibition of all reducing power of the support appears to present the most serious problem. Investigation of a variety of supports is continuing.

An important advantage of an extraction chromatography system based upon HD(DIBM)P rather than upon HDEHP is that for columns holding oxidized Am equally well against an aqueous HNO_3 phase containing approximately

$0{\cdot}2\,F\,S_2O_8^{-2}$, the HD(DIBM)P column permits the more ready removal of Am(III) by an aqueous acid phase containing no $S_2O_8^{-2}$. For example, Hulet[14] reported difficulty in removing Am from his HDEHP column, stating: "Reducing and stripping americium from the stationary organic phase was erratic and slow for undetermined reasons". For comparison, the approximate K values for Am(III) in the 0·3 F extractant in *n*-heptane vs. 0·025 M HNO_3 are: HDEHP (1×10^3), HD(DIBM)P (2×10^{-3}).

The K values for Cm(III) and the other pertinent M(III) elements reported in Table 1 are too low to permit a systematic study of the extraction stoichiometry in terms of dependence upon the concentration of HD(DIBM)P in the extractant phase and the concentration of hydrogen ion in the aqueous; and the incomplete oxidation of americium prevents exact elucidation of the stoichiometry involved in the extraction of oxidized americium.

But from the results of an analogous study of the extraction of Am(III)[17] and U(VI)[18] in the system HDEHP in toluene vs. an aqueous HCl or $HClO_4$ phase possible respective stoichiometries of extraction of Cm(III) and of "oxidized americium" assuming it to be Am(VI) may be represented as:

$$Cm_A^{+3} + 3(HY)_{2_O} \rightleftharpoons Cm(HY_2)_{3_O} + 3H_A^+ \qquad (1)$$

$$AmO_2{}^{+2}{}_A + 2(HY)_{2_O} \rightleftharpoons AmO_2(HY_2)_{2_O} + 2H_A^+ \qquad (2)$$

where HY represents HD(DIBM)P and the subscripts A and O refer respectively to the mutually equilibrated aqueous and organic phases.

Operationally, as seen in Table 2, both the extractant dependency and the inverse hydrogen ion dependency of the observed K for americium are more nearly first power than second. But in evaluating these operational dependencies it should be noted that the H^+ concentrations reported were initial not final values, that the americium was quite certainly not quantitatively oxidized, and that there was an indeterminate depression of the extraction of oxidized americium through aqueous phase complexing by sulfate[14, 16] and/or persulfate which probably differed among the various experiments.

The importance of "pre-oxidizing" the extractant phase (both extractant and diluent), the aqueous phase used as feed and as scrub, and the physical contacting equipment used cannot be over emphasized. Failure to take these precautions may lead to failure to oxidize the americium or to maintain it in its oxidized state. Although the requirements for maintaining these strongly oxidizing conditions are stringent, it should not prove difficult to meet them in practice, either in large-scale nuclear technology or in small-scale experimentation.

The need for removal of traces of HD(DIBM)P from aqueous Am and Cm product phases should also be emphasized. If these traces are not removed, interference may be experienced in studies of these products or in further processing of them.

---

17. D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, *J. inorg. nucl. Chem.* **7**, 276 (1958).
18. D. F. Peppard, G. W. Mason, I. Hucher and F. A. J. A. Brandao, *J. inorg. nucl. Chem.* **24**, 1387 (1962).

Finally, in considering any modification of the separations process as described it should be recalled that the *K* values for Cm(III) and other M(III) actinides and lanthanides are extremely low because of the depressant action of the particular aqueous phase employed. If the oxidation of americium is accomplished by different means so that this depressant action is not present the *K* values for these M(III) elements will be much higher.

Acknowledgements—The authors wish to thank Dale Henderson of the Chemistry Division of Argonne National Laboratory for performing the alpha pulse analyses which served to establish the Am/Cm ratios, by activity, in the product phases reported in Table 2.