ANL-6999

MAY 14 1969

ANL-6999

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NITRIC ACID-ORGANIC SOLVENT MIXTURES FOR SEPARATION OF PLUS-THREE ACTINIDES ON ANION RESINS

I. Survey of Solvents

by

D. C. Stewart, C. A. A. Bloomquist,
and J. P. Faris

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Chemistry Division

February 1965

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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ABSTRACT

More than 60 water-miscible organic solvents have been surveyed for use as possible components in mixed solvent-nitric acid elutriants to accomplish transplutonium element separations in anion-exchange resin systems. Several solvents for accomplishing such separations were found, nine of which met preliminary criteria established to determine their suitability for hot-cell use with high levels of radiation. Americium-curium separation factors superior to those of previously reported systems were found in a number of the solvent mixtures. Several solvents were also discovered having promising potentiality for the difficult americium-promethium separation.

INTRODUCTION

The use of mixed organic liquid-aqueous acid elutriants for anion resin column separation of various elements has received considerable attention recently, particularly by J. Korkisch and his co-workers at the University of Vienna. A paper from Argonne by Faris and Warton,⁽¹⁾ using nitric acid-methanol mixtures as elutriants, described the separation from each other of the individual light rare-earth elements (lanthanum to terbium). Because of the similarity in chemical behavior between the plus-three transplutonium elements and the rare earths, it would be expected that the same system could be used for certain actinide element separations, an expectation that was later justified by the excellent separation of americium and curium demonstrated by Hines, Wahlgren, and Lawless.⁽²⁾

The results reported by these last authors strongly suggest that the mixed organic-aqueous acid systems have considerable potential for the entire area of transplutonium element processing. Unlike most ion-exchange methods used to date to separate the chemically similar rare-earth fission

products from the transplutoniums, and that group of elements from each other, no corrosive or highly salted reagents are required, no precise control of pH is needed, the columns are operated at room temperature, the elutriant materials are easily available in high purity and are relatively inexpensive, and the products are obtained in a solution from which they can readily be recovered. Since transplutonium element processing typically requires isolation of microgram quantities of the heavier elements from grams of associated target material, this last point, ease of recovery, is a major advantage.

The methanol system, however, has drawbacks for operations with high levels of radioactivity, primarily because of the fire hazard that its use would involve. Several authors have demonstrated that certain other organics (other monohydric alcohols, acetone, etc.) produced distribution ratios that were effective for fractionation of the light rare earths in the organic-nitric acid-anion resin system, but most of these other solvents tested also have high volatilities and low flash points. It was accordingly decided to make a "shot-gun" survey of as many as possible available solvents having the required water miscibility to see if others with high flash points and low volatilities could be found producing the same effect as methanol. Selected promising solvents uncovered during this survey will then be studied in more detail for application to actual transplutonium element-separation processes. Of particular concern are possible drawbacks such as deleterious effects on separations caused by radiation or prolonged contact with nitric acid, slowness in reaching equilibrium, change of K_D with macro loading of the columns, etc.

There were also several secondary purposes to the survey. Comparison of the Faris and Warton data with those of Hines, Wahlgren, and Lawless would indicate that americium in a methanol-nitric acid system would elute in approximately the neodymium-promethium position; that is, that the elution positions of the heavier actinide series are displaced downward with respect to their rare-earth homologues, indicating that a group separation of actinides from rare-earth fission products would not be possible using methanol. It was hoped that other solvents might cause a lesser or no displacement of the two series, thus permitting a single-step actinide-lanthanide fission product separation. Also, in the methanol system, the rare earths heavier than terbium elute quickly with very little separation. Where the rare earths as a group show a higher affinity for the resin than in methanol, there conceivably would be the possibility of separation of the individual heavier members of the series. It was known from the work of Faris and Warton and of Marple⁽³⁾ that systems giving higher rare-earth K_D 's than methanol did exist, and it was hoped to find others during this survey. In addition to these two interests, there was also the general purpose of obtaining a better understanding of the mechanisms involved in the very interesting mixed-solvent systems themselves.

The survey described in this report had three separate phases. In the first, Faris used his column elution-spectrographic analysis technique to compare certain solvents directly to the methanol system, using inert rare earths as stand-ins for the actinides. The second phase involved the batch determination of distribution ratios for americium between 90% solvent, 10% 5M HNO_3 and Dowex 1 nitrate form resin for a large group of organics miscible in water. In the third phase, certain promising solvents found in the first two sets of experiments were used to determine batch distribution ratios for curium (to evaluate separation possibilities within the actinide group) and for promethium, terbium, and thulium (to determine the relative actinide-lanthanide positions and to evaluate possible separations within the heavy rare-earth group). Radioactive tracer techniques were used for all the batch experiments in the last two phases, as is described below.

PHASE 1 - SPECTROGRAPHIC APPROACH

Details of this method of determination of distribution ratios (K_D values) are given by Faris and Warton.⁽¹⁾ In essence, a mixture of inert rare earths is eluted through a resin bed containing a known amount of anion resin (Dowex 1, X4), and fractions of the eluate are spectrographically analyzed as they come off the column. Elution peak positions for the individual rare earths can be estimated quite closely, and K_D values calculated from the column-operation theory of Mayer and Tompkins.⁽⁴⁾ (K_D = element concentration per gram of resin/concentration per milliliter of elutriant.) While the method does not yield as precise values as batch-equilibration studies, it has the advantage that, if desired, distribution ratios for the entire series of rare earths, or for any other group of elements, can be rapidly obtained in a single experiment under known-to-be-uniform conditions.

Table I presents K_D values obtained by this technique, and compares them to the results obtained with the methanol-nitric acid system. It will be seen that ethanol, Cellosolve, and methanol-amyl acetate mixtures all appear to give higher K_D values for the rare earths when they are substituted for methyl alcohol in a 90% solvent, 10% aqueous nitric acid system. Preliminary experiments (data not given) indicated that isopropyl alcohol and acetone were also superior to methanol in causing rare-earth absorption onto the resin.

Table I
K_D VALUES BY THE COLUMN ELUTION-SPECTROGRAPHIC ANALYSIS TECHNIQUE

Elutriant	K _D Values											
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy-Yb	Lu	Y	Sc
90% Methanol 10% 7M HNO ₃	10,300	5,850	3,400	1,510	230	116	63	46	38-29	29	29	52
90% Cellosolve 10% 7M HNO ₃	A	A	A	A	A	133	78	43	38-33		33	7
90% Dioxane 10% 3M HNO ₃	A	A	A	A	105	80	64	59	54-45		54	22
90% Tetrahydrofuran 10% 3M HNO ₃	85	72	60	50	37	30	30	30	30-20		25	10
50% Methanol 40% Amyl Acetate 10% 7M HNO ₃	A	A	A	A	A	A	110	76	65-52	50	57	12
60% Methanol 30% Amyl Acetate 10% 7M HNO ₃	A	A	A	A	A	A	A	A	90-82		85	27
80% Methanol 10% Acetic Acid 10% 7M HNO ₃	A	A	A	A	79	52	29	23	20-17	17	17	4
90% Ethyl Lactate 10% 5M HNO ₃	~90	~90	~90	38	22	22	22	18	18		20	17
90% Dimethyl Formamide 10% 5M HNO ₃	No adsorption											
90% Diethylene Glycol Dimethyl Ether 10% 5M HNO ₃	A	A	A	115	80	30	24	14	18		23	12
90% Ethylene Glycol Monobutyl Ether 10% 5M HNO ₃	A	A	A	A	100	88	75	50	80-60		80	35
90% Dimethylene Glycol Monomethyl Ether 10% 5M HNO ₃	A	A	A	160	48	48	30	18	35-20		19	13
90% Diethylene Glycol Monoethyl Ether 10% 5M HNO ₃	130	90	50	20	11	11	11	11	12-10		10	10
90% Ethanol 10% 5M HNO ₃	A	A	A	A	A	700	410	220	210-185	160	180	35

A = Absorbed.

PHASES 2 AND 3 - BATCH EQUILIBRATIONS, EXPERIMENTAL

Resin. A one-pound lot of nitrate form Dowex 1 (Bio Rad AG1-X4) resin, 200-400 mesh, was further treated with a series of batch contacts with 3M HNO₃ until chloride ion could no longer be detected in the contacting solution. The resin was then thoroughly washed with deionized distilled water and dried for 36 hr at 70-77°C, following which it was transferred back to the amber bottle in which it was received, and the closed bottle kept in a desiccator when not in use. A water analysis of the dried resin by a D₂O spiking technique gave a value of 0.71%.

Solvents. Solvents were used off the shelf, with no attempt at further purification. Since some of the organics in their commercial form contain water, some of the distribution systems as studied were not strictly 90% organic, 10% aqueous.

Tracers. The following radioactive tracers were used: Am^{241} , Cm^{244} , Pm^{147} , Tb^{160} , and Tm^{170} . Standard counting methods were used for their measurement.

Procedure. Three separate approximately 100-mg amounts of the dried resin were accurately weighed on an analytical balance into screwcap-stoppered 13-ml centrifuge tubes for each determination. (Aluminum foil inserts were used in the plastic caps to limit contact with the organic solvents.) Elutriant was prepared by pipetting 1 ml of 5.0M HNO_3 into a 10-ml volumetric flask, adding the tracer being studied as 25 μl of 1M HNO_3 solution, and filling the flask to the mark with the solvent under consideration. After mixing, 3 ml of the elutriant were placed in each of the tubes and the tubes were capped.

Equilibration was carried out by rotating the tubes on a syringe rotator. A preliminary experiment on an ethanol system carried out over an 8-hr period indicated that equilibrium was reached in less than one hour, so this time was selected as the standard mixing interval for all systems. Equilibrations were at room temperature (24-26°C). Following equilibration, the resin was centrifuged to the bottom of the tubes and each supernatant was assayed in duplicate by pipetting aliquots onto platinum plates for counting. The number of counts of tracer going onto the resin was calculated from the difference between the initial and final elutriant tracer concentrations, and K_D values were computed in the usual manner.

Since this was a scouting experiment, extremely high precision was not sought for the K_D values. If the solvent was obviously not particularly promising for further consideration (low distribution values, high viscosity leading to handling problems, etc.), the first three K_D values measured were averaged. If the solvent showed more promise, measurements were made until a reasonably consistent set of values was obtained.

RESULTS

As described above, Phase 2 of the survey consisted of determination of K_D values for americium plus-three ion in systems consisting of 90 v/o of the test solvent, 10 v/o of 5.0M HNO_3 . Results of this series of experiments are presented in Table II, the data of which permitted the immediate elimination of certain solvents. Physical properties of the remaining organic materials are given in Table III. Data for Table III were, in general, taken from Mellan⁽⁵⁾ or Marsden,⁽⁶⁾ although in a few cases the figures were taken from literature issued by the manufacturers.

Table II
K_D VALUES FOR AMERICIUM

Solvent	Source and Grade	Formula	(K _D) _{Am}	Number of Determinations	Comments
<u>Monohydric Alcohols</u>					
Methyl	Mallinkrodt - analytical reagent	CH ₃ OH	535 ± 5	3	Standard Test System: 90% Solvent, 10% 5M HNO ₃ .
Ethyl	U.S.I. - absolute reagent	CH ₃ CH ₂ OH	6065 ± 419	10	
n-propyl	Fisher - reagent	CH ₃ CH ₂ CH ₂ OH	2442 ± 67	3	
Isopropyl	Mallinkrodt - analytical reagent	CH ₃ CH(OH)CA ₃	5363 ± 1240	8	
n-butyl	Baker & Adamson - reagent	CH ₃ (CH ₂) ₂ CH ₂ OH	438 ± 84	3	
Isobutyl	Merck - ?	(CH ₃) ₂ CHCH ₂ OH	756 ± 32	3	
Sec-butyl	Matheson - ?	CH ₃ CH ₂ CH(OH)CA ₃	866 ± 144	3	
Tert-butyl	Fisher - reagent	(CH ₃) ₃ COH	3390 ± 550	3	
Primary n-amyl	Matheson - practical	CH ₃ (CH ₂) ₃ CH ₂ OH	273 ± 50	3	
	Fisher - reagent		292 ± 76	9	
Sec-n-amyl	Matheson - practical	CH ₃ CH ₂ CH(OH)CH ₂ CH ₂ OH	588 ± 82	8	M.P. ≈ 25°C
Tert-amyl	Fisher - reagent	C ₂ H ₅ COH(CH ₃) ₂	785 ± 134	3	Commercial product is mixture of isomers.
3-Methoxy Butanol	Eastman - practical	CH ₃ CH(OCH ₃)CH ₂ CH ₂ OH	1455 ± 148	3	Mixture of isomers.
2-Isobutoxy Ethanol	Baker - practical	(CH ₃) ₂ CHCH ₂ OCH ₂ CH ₂ OH	350 ± 8	3	
Diacetone Alcohol	Fisher - technical	(CH ₃) ₂ COHCH ₂ COCH ₃	537 ± 55	3	Reacts with acid. (See text.)
Allyl Alcohol	Matheson - laboratory or manufacturing	CH ₂ = CHCH ₂ CH ₂ OH	881 ± 7	3	Toxic.
2 Mercapto Ethyl Alcohol	Eastman - for chemical purposes	HSCH ₂ CH ₂ OH	504 ± 10	3	
Trifluoroethanol	Pennsalt - industrial	CF ₃ CH ₂ OH	1417 ± 280	6	Heavier than resin. Somewhat toxic.
C-3 Fluoroalcohol	Dupont - technical	HCF ₂ CF ₂ CH ₂ OH	1562 ± 26	3	Heavier than resin.
Benzyl Alcohol	Merck - reagent	C ₆ H ₅ CH ₂ OH	305 ± 3	3	Some dissolving effect on resin.
Cyclohexanol	Matheson - laboratory or manufacturing	CH ₂ (CH ₂) ₄ CHOH	123 ± 24	7	Viscous.
Tetrahydrofurfuryl Alcohol	Matheson - laboratory or manufacturing		7.2 ± 0.9	3	Reacts slowly with HNO ₃ to give yellow color.
<u>Glycols, Polyhydric Alcohols, etc.</u>					
Ethylene Glycol	Matheson - laboratory or manufacturing	HOCH ₂ CH ₂ OH	0	3	Viscous, hygroscopic.
Propylene Glycol	Fisher - USP	CH ₃ CHOHCH ₂ OH	3.5 ± 0.2	3	
1,5 Pentanediol	Eastman - practical	HOCH ₂ (CH ₂) ₃ CH ₂ OH	934 ± 229	8	Very viscous.
Glycerol	Baker - reagent	CHOH(CH ₂ OH) ₂	0.3	3	
Polyethylene Glycol	Allied Chemical	-	44 ± 8	3	
2 Methyl-2,4-Pentanediol	Eastman - for chemical purposes	(CH ₃) ₂ COHCH ₂ CHOHCH ₃	1046 ± 92	7	"Diolane," "Hexylene Glycol," viscous.
Ethylene Glycol Monomethyl Ether	Fisher - reagent	CH ₃ OCH ₂ CH ₂ OH	239 ± 3	3	"Methyl Cellosolve."
Ethylene Glycol Monoethyl Ether	Fisher - purified	C ₂ H ₅ OCH ₂ CH ₂ OH	765 ± 31	3	"Cellosolve."
Ethylene Glycol Monobutyl Ether	Fisher - purified	C ₄ H ₉ OCH ₂ CH ₂ OH	305 ± 12	3	"Butyl Cellosolve," toxic.
Diethylene Glycol	Fisher - reagent	HOCH ₂ CH ₂ OCH ₂ CH ₂ OH	3.0 ± 0.3	3	Extremely viscous, hygroscopic.
Dipropylene Glycol	Eastman - practical	CH ₃ CHOHCH ₂ OCH ₂ CHOHCH ₃	20 ± 1	3	Extremely viscous.
Diethylene Glycol Monomethyl Ether	Fisher - purified	CH ₃ OCH ₂ CH ₂ OCH ₂ CH ₂ OH	137 ± 3	3	"Methyl Carbitol."
Diethylene Glycol Monoethyl Ether	Fisher - purified	C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ CH ₂ OH	31 ± 4	3	"Carbitol," viscous, hygroscopic.
Diethylene Glycol Monobutyl Ether	Fisher - purified	C ₄ H ₉ OCH ₂ CH ₂ OCH ₂ CH ₂ OH	270 ± 7	3	"Butyl Carbitol," viscous.
Triethylene Glycol	Fisher - purified	(HOCH ₂ CH ₂ OCH ₂) ₂	20 ± 0.3	3	Viscous.
Triethylene Glycol Dimethyl Ether	Eastman - practical	CH ₃ O(CH ₂) ₂ O(CH ₂) ₂ OCH ₃	214 ± 1	3	
Diethylene Glycol Monoethyl Ether Acetate	Eastman - practical	C ₂ H ₅ O(CH ₂) ₂ O(CH ₂) ₂ OCOCH ₃	1790 ± 405	6	"Carbitol Acetate," very low vapor pressure.
Ethylene Glycol Monoethyl Ether Acetate	Eastman - practical	CH ₃ COO(CH ₂) ₂ OC ₂ H ₅	12 ± 0.3	3	"Cellosolve Acetate."
Benzyl Glycol	Eastman - for chemical purposes	C ₆ H ₅ CH ₂ OCH ₂ CH ₂ OH	88 ± 3	3	
<u>Ketones</u>					
Acetone	Baker & Adamson - reagent	CH ₃ COCH ₃	786 ± 13	3	
Methyl Ethyl Ketone	Mallinkrodt - reagent	CH ₃ COC ₂ H ₅	410 ± 57	3	
<u>Acids</u>					
Acetic (Glacial)	Baker - reagent	CH ₃ COOH	1716 ± 28	3	
Propionic	Eastman - for chemical purposes	CH ₃ CH ₂ COOH	2241 ± 80	3	

Table II (Contd.)

Solvent	Source and Grade	Formula	(K _D) _{Am}	Number of Determinations	Comments
<u>Acids (Contd.)</u>					
Lactic Acid (dl)	Baker - reagent	CH ₃ CHOHCOOH	0.6 ± 0.4	6	Commercial product is 85% acid.
β-Mercaptopropionic Acid	Evans Chemetics - ?	HSCH ₂ CH ₂ COOH	513 ± 12	3	Melting point, 17-19°C, gradual reaction in system.
Dichloromonofluoro Acetic Acid	Allied Chemical - practical	Cl ₂ FCCOOH	109 ± 2	3	Heavier than resin.
Perfluoropropionic Acid	3M Co. - ?	CF ₃ CF ₂ COOH	356 ± 5	3	Heavier than resin.
Perfluorobutyric Acid	3M Co. - ?	CF ₃ CF ₂ CF ₂ COOH	367 ± 12	3	Heavier than resin.
Kel-F Acid 683	M. W. Kellogg Co. - for manufacturing use	Cl(CF ₂ CFCl) ₂ CF ₂ COOH	422 ± 16	3	Viscous. Heavier than resin.
Kel-F Acid 8114	M. W. Kellogg Co. - for manufacturing use	Cl(CF ₂ CFCl) ₃ CF ₂ COOH	1195 ± 290	3	Extremely viscous. Heavier than resin.
<u>Miscellaneous</u>					
Ethyl Lactate	Matheson - laboratory or manufacturing	CH ₃ CHOHCOOC ₂ H ₅	51 ± 0.7	3	
n-butyl Lactate	Matheson - laboratory or manufacturing	CH ₃ CHOHCOOC ₄ H ₉	57 ± 0.7	3	
Tetrahydrofurfuryl Acetate	Matheson - laboratory or manufacturing		3174 ± 61	3	
p-dioxane	Eastman - for chemical purposes		177 ± 7	3	
Dimethyl Formamide	Merck - reagent	HCON(CH ₃) ₂	11 ± 2	3	
Dimethyl Sulphoxide	Fisher - reagent	CH ₃ SOCH ₃	7.3 ± 0.4	3	

Table III

PHYSICAL PROPERTIES OF POSSIBLY USEFUL SOLVENTS

Solvent	Solubility of Solvent in H ₂ O	Boiling Point, °C (760 mm Hg)	Flash Point		Specific Gravity		Viscosity (centipoises)	
			Value, °F	Type	Value	Temp, °C	Value	Temp, °C
Methyl Alcohol	Miscible	64.5	60	Open cup	0.7924	20	0.59	20
Ethyl Alcohol	Miscible	78.32	61	Open cup	0.7851	25	1.22	20
n-propyl Alcohol	Miscible	97.15	90	Open cup	0.8050	20/20	2.256	20
Isopropyl Alcohol	Miscible	82.3	70	Open cup	0.7862	20/20	2.4	20
n-butyl Alcohol	20 w/o (20°C)	117.7	115	Open cup	0.811	20/20	2.948	20
Isobutyl Alcohol	20 v/o (25°C)	107.9	103	Open cup	0.8034	20/20	6.68	20
Sec-butyl Alcohol	60 w/o (20°C)	99.5	80	Open cup	0.8079	20/20	3.78	20
Tert-butyl Alcohol	Miscible	82.36	~60	Open cup	0.783	25/25	3.316	30
Primary n-amyl Alcohol	9.2 w/o (25°C)	137.8	135	Open cup	0.82	20/20	3.31	25
Sec-n-amyl Alcohol	9.1% v/o (30°C)	115.6	100	Closed cup	0.82	20	4.12	25
3-Methoxy Butanol	Miscible	161.1	165	-	0.924	20/20	-	-
1-5 Pentanediol	-	239.4	-	-	0.994	20/20	-	-
2-Mercapto Ethyl	Miscible	156.9	170	Open cup	1.1168	20/20	3.4	20
Trifluoroethanol	Miscible	74.05	90	Open cup	1.387	22/25	1.996	20
C-3 Fluoroalcohol	Very soluble	110	120	Open cup	1.485	20	-	-
Cellosolve	Miscible	131.5	135	Open cup	0.9311	20/20	2.05	20
Hexylene Glycol	Miscible	198.3	200	-	0.924	15.5/15.5	38.4	20
Butyl Cellosolve	-	171.3	165	Open cup	0.9019	20/20	6.42	20
Carbitol Acetate	Miscible	217.7	230	Open cup	1.0114	20/20	-	-
Acetone	Miscible	56.2	15	Open cup	0.7911	20/4	0.316	25
Methyl Ethyl Ketone	12 w/o (23°C)	79.57	22	Open cup	0.8051	20/4	0.417	21.3
Acetic Acid	Miscible	118.1	110	Open cup	1.049	20/4	-	-
Propionic Acid	Miscible	141.1	-	-	0.992	-	-	-
Tetrahydrofurfuryl Acetate	Miscible	196.0	190	Closed cup	1.064	20/20	-	-

The final phase of the experimental work then consisted of making a still smaller selection of the more interesting possibilities from the solvent group given in Table III for testing with curium and the three rare-earth tracers. Results of these experiments are presented in Table IV. The separation factor as used in this table is defined as

$$\alpha_{\text{Cm}}^{\text{Am}} = \frac{(K_D)_{\text{Am}}}{(K_D)_{\text{Cm}}}, \text{ etc.}$$

This alpha factor, as so defined, corresponds from the Mayer and Tompkins theory to the milliliters of elutriant passed at the americium elution peak in a column operation, divided by the milliliters passed at the curium elution peak (each volume corrected by subtracting one free-column volume to compensate for the solution in the column below the initial starting absorption band at the start of the experiment).

Table IV
SEPARATIONS DATA FOR SELECTED SOLVENT-AQUEOUS SYSTEMS

Solvent	K_D Values					Separation Factors (α)			
	Am^{241}	Cm^{244}	Pm^{147}	Tb^{160}	Tm^{170^*}	Am/Cm	Pm/Cm	Tb/Cm	Am/Pm
Ethyl Alcohol	6065	2176 $\pm$ 178	5165 $\pm$ 363	170 $\pm$ 25	258 $\pm$ 5	2.79	2.38	0.13	1.17
Isopropyl Alcohol	5363	1884 $\pm$ 91	5401 $\pm$ 607	225 $\pm$ 9	479 $\pm$ 14	2.84	2.87	0.12	0.994
n-propyl Alcohol	2442	1075 $\pm$ 17	2137 $\pm$ 255	140 $\pm$ 3	215 $\pm$ 36	2.27	1.99	0.14	1.13
3-methoxy-1-butanol	1455	373 $\pm$ 102	1753 $\pm$ 140	96 $\pm$ 13	45 $\pm$ 6	3.90	4.70	0.26	0.83
Trifluoroethanol	1417	635 $\pm$ 20	1249 $\pm$ 13	65 $\pm$ 8	90 $\pm$ 3	2.23	1.97	0.10	1.13
C-3 Fluoroalcohol	1562	589 $\pm$ 15	1191 $\pm$ 46	-	-	2.66	2.02	-	1.31
Hexylene Glycol (Diolane)	1046	597 $\pm$ 72	1818 $\pm$ 331	118 $\pm$ 5	214 $\pm$ 10	1.75	3.04	0.19	0.58
Cellosolve	765	308 $\pm$ 1	821 $\pm$ 24	37 $\pm$ 1	31 $\pm$ 1	2.48	2.66	0.12	0.93
Carbitol Acetate	1790	1077 $\pm$ 178	4548 $\pm$ 448	222 $\pm$ 26	96 $\pm$ 3	1.67	4.13	0.21	0.40
Glacial Acetic Acid	1716	840 $\pm$ 32	1518 $\pm$ 40	120 $\pm$ 4	147 $\pm$ 3	2.05	1.81	0.14	1.13
Propionic Acid	2241	991 $\pm$ 40	1734 $\pm$ 97	179 $\pm$ 13	403 $\pm$ 5	2.26	1.75	0.18	1.29
Tetrahydrofurfuryl Acetate	3174	1690 $\pm$ 14	1200 $\pm$ 41	151 $\pm$ 10	48 $\pm$ 3	1.88	0.71	0.09	2.64

*See text.

DISCUSSION

The data of Table II indicate that a gratifyingly large number of solvents can be used in place of methanol to cause americium plus-three ion to be absorbed from organic-low nitric acid concentration mixtures. This result, of course, was not entirely unexpected because of the previous experience of Faris and Warton, with rare earths using organics other than methanol; of Korkisch and Arrhenius,⁽⁷⁾ with acetic or propionic acids mixed with nitric acid; of Korkisch and Urubay,⁽⁸⁾ with straight-chain alcohols other than MeOH; of Fritz and Greene⁽⁹⁾ and Marple,⁽³⁾ with isopropyl alcohol-nitric acid mixtures; *et al.*

Even small amounts of impurities in the solvents tested may possibly markedly affect the K_D values determined in experiments at tracer-level concentrations, so extensive generalizations probably cannot be safely made from the data of Table II since unpurified solvents were used throughout this survey. If, however, the numbers are accepted at face value, a few tentative comments may be made. (Figures in parentheses in the following paragraphs are americium distribution ratios from Table II.)

Monohydric Alcohols

As a group, the monohydric alcohols appear to be particularly effective in promoting americium absorbability in the organic solvent-nitric acid-anion resin system. Many of them, of course, would be too much of a fire hazard to be considered for hot-cell work, but conceivably could have utility for tracer scale or inert rare-earth separations.

Diacetone alcohol was first thought to be a promising solvent because of its high flash point (155°F), but it became evident that it was reacting rapidly with the nitric acid, making it impossible to reproduce distribution-ratio data. Furfuryl alcohol was tried, but hurriedly abandoned when it reacted explosively on contact with the acid.

1. The unsubstituted straight-chain monohydric alcohols show an interesting but puzzling pattern:

Methyl (535) < Ethyl (6065) > Propyl (2442) >
n-butyl (440) > primary n-amyl (292)

Korkisch and Janauer⁽¹⁰⁾ believe that substitution of an organic liquid for water in an ion-exchange system produces the observed effects by a complex interaction of the following variables: (a) solvent uptake and swelling by the resin, (b) effects on dissociation, (c) solvation effects (dehydration of hydrated ions), (d) effects on complex ion formation, and (e) ionic and molecular interactions. Certainly it is difficult to invoke any single one of these effects to explain why ethyl alcohol should be so much more efficient in increasing americium absorption as compared to the members of the series on either side of it.

2. Side chains appear to increase the K_D values:

n-propyl (2442)	n-butyl (440)
isopropyl (5363)	isobutyl (756)

3. Secondary alcohols appear to be more effective than primaries:

n-butyl (440)	n-amyl (242)
sec-butyl (866)	sec-n-amyl (588)

4. For ethyl alcohol, all the alpha carbon substituents considered produce an inhibitory effect:

Ethyl alcohol (6065)
 Mercapto ethyl alcohol (504)
 2-isobutoxy ethanol (350)
 Benzyl alcohol (305)
 Tetrahydrofurfuryl alcohol (7.2)

5. Substitution of fluorine for hydrogen atoms on the alpha carbon of ethyl alcohol and on the α and β carbons of propanol also causes a drop in americium K_D values:

Ethyl (6065)	n-propyl (2442)
Trifluoroethyl (1417)	C-3 fluoro (1562)

6. On the basis of very limited data, a double bond in the aliphatic chain of an alcohol seems to increase K_D values, as does a methoxy substituent:

n-butyl (440)
 Allyl (881)
 3-methoxy butanol (1455)

7. In the present investigation, ethyl alcohol was found to be more effective than isopropyl alcohol in promoting americium absorbability, which is the opposite of the effect observed by Marple⁽³⁾ with lanthanum. Both alcohols were found to be highly effective in both cases, however, and the apparent contradiction may simply be due to differences in solvent purity.

Glycols and Derivatives; Polyhydric Alcohols

While members of this group as a whole proved to be somewhat disappointing in their action, as far as increasing americium absorbability was concerned, several of the solvents (Cellosolve and diethylene glycol mono-ether acetate) are of some interest, as will be discussed later. "Hexylene glycol" and 1,5-pentanediol conceivably could be useful if an appropriate diluent could be found to decrease their viscosity while still retaining their effect on the americium K_D value; 1,2,6-hexanetriol was too viscous to be tested, and dibutyl Carbitol formed two phases when mixed with the nitric acid.

1. In the unsubstituted glycols, increasing the chain length between the two end hydroxyl substituents appears to increase the K_D values, the effect being more marked if the intermediate chain is entirely aliphatic:

Ethylene glycol (0)	Ethylene glycol (0)
Diethylene glycol (3)	1,5-pentanediol (934)
Triethylene glycol (20)	

2. Conversion of the unsubstituted glycol to an ether improves americium absorbability on the resin. Conversion of the glycol-ether to a glycol-ether-ester causes inhibition in the case of "Cellosolve acetate," but a marked improvement for "Carbitol acetate":

	Ethylene glycol (0)	Diethylene glycol (3)	Trimethylene glycol (0)
monomethyl ether	(239)	(137)	-
monoethyl ether	(765)	(31)	-
monobutyl ether	(305)	(270)	-
dimethyl ether	-	-	(214)
monoethyl ether acetate	(12)	(1790)	-

Aldehydes and Ketones

The very limited number of water-miscible solvents in this group makes it impossible to comment even in a speculative fashion on their action in the investigated system. Acetylacetone, acetaldehyde, and propionaldehyde were all tried but formed two phases when mixed with the nitric acid.

Acids

Acetic and propionic acids were the most effective agents of those investigated in this group. Because of its reactivity with nitric acid, formic acid could not be tested. (Korkisch and Urubay⁽⁸⁾ have studied formic acid-organic solvent mixtures in anion-resin systems, but with no added mineral acid. Korkisch and his co-workers have similarly used acetic acid, its chloroderivatives, propionic acid, di- and tricarboxylic acids, etc., particularly in examining uranium-thorium-rare-earth separations.)

Glacial acrylic and glacial methacrylic acids formed two phases on contact with the acid and could not be tested. Commercial lactic acid contains 10-15% water, so the test system in this case was not strictly 10% aqueous, 90% organic.

The americium distribution data for carboxylic acid effects are somewhat limited. However, a β carbon substitution of a mercapto group, or a complete substitution of either fluorine or chlorine atoms for the hydrogens on noncarboxylic carbons in acetic and propionic acids, decreases americium absorbability:

Acetic acid (1716)	Propionic acid (2241)
Dichloromonofluoro-	Perfluoropropionic
acetic acid (109)	acid (356)
	β -mercaptopropionic
	acid (513)

The high densities of the fluoro-acids makes their potential usefulness for actinide separations doubtful, since the resin tends to float in the elutriant. There would also be a question with respect to their resistance to radiation, since decomposition would presumably result in the release of free fluorine.

Miscellaneous Group

Only one of the compounds tested in this category (tetrahydrofurfuryl acetate) shows much promise in terms of the purposes of the present investigation. It, however, seems well worth further investigation in view of its strong effect on americium absorbability ($K_D = 3174$).

An arbitrary set of requirements for solvents for use in hot-cell operations was established: (1) effect on americium absorbability comparable to or greater than methanol (americium $K_D > 500$), (2) open-cup flash point 110°F or higher, (3) specific gravity 1.1 or lower, (4) viscosity and reactivity with nitric acid to give no handling problems as judged by experience during the batch experiments, and (5) no excessive toxicity problems as determined by a brief review of the literature. Applying these criteria to the data of Tables II and III leaves nine remaining solvents: n-butyl alcohol, n-amyl alcohol, 3-methoxy butanol, 2-mercapto ethyl alcohol, Cellosolve, Carbitol acetate, acetic acid, propionic acid, and tetrahydrofurfuryl acetate. In addition, hexylene glycol and 1,5-pentanediol could possibly be made useful by appropriate dilution with one of the other solvents to reduce viscosity. The results of this portion of the work are thus satisfactory for the main purpose of the survey, that of finding a solvent presenting less fire hazard than does methanol for hot-cell work.

Table IV presents K_D values for curium and the three rare-earth tracers in a representative group of solvents chosen from Table II, and also lists separation factors calculated for the various elements. Comments will be made below on the rare-earth data, but the major point of interest is the uniformly excellent americium-curium separations that appear to be possible in organic solvent-aqueous nitric acid-anion resin systems. In most cases, the americium-curium separation factor is greater than 2. (This was corroborated in the ethanol system by a batch experiment in which both Am^{241} and Cm^{244} tracers were present. K_D 's for the two elements were obtained from pulse-analysis data taken on the supernatant after equilibration.)

For comparison, Table V lists separation factors taken from the literature for all the ion-exchange resin systems reported to have been applied to the problem of americium-curium purification. The mixed solvents are

seen to be exceptionally promising for americium-curium separations, although, since it is known that separations with mixed solvent elutriants drop off rapidly for elements heavier than terbium in the rare-earth series, separation of the heavier actinides may also be poorer. In general, however, the actinide elements elute earlier than their lanthanide homologues, so it is probable that good separation factors will be maintained further into the heavier element range for actinides than for lanthanides. (Hines, Wahlgren, and Lawless⁽²⁾ report a curium/californium separation factor of 0.37 in the methanol-nitric acid system.) Separations through californium will probably be feasible, but other types of ion-exchange systems may be superior for transcalifornium elements.

Table V
SEPARATION FACTORS FROM THE LITERATURE

Eluting Solution	Separation Factor (α)		
	Am/Cm	Am/Pm	Reference
<u>Cation Resin Systems</u>			
Citrate, room temp	1.18	1.03	(11)
Citrate, 87°C	1.18	-	(12),(15)
Glycolate, room temp	1.23	0.98	(13)
Glycolate, 87°C	1.24	0.92	(13)
	1.14	-	(14)
Lactate, room temp	1.21	0.97	(16)
Lactate, 87°C	1.19	0.97	(16)
	1.27	0.97	(22)
	1.21	-	(14),(15)
Tartrate, room temp	1.30	0.89	(16)
Tartrate, 60 to 100°C	1.08 to 1.21	0.82 (100°C)	(16)
Hydroacrylate, room temp	1.13	-	(16)
α Hydroxy Isobutyrate, room temp	1.39	1.21	(18)
α Hydroxy Isobutyrate, 77°C	1.38	-	(25)
α Hydroxy Isobutyrate, 87°	1.45	-	(14)
	-	1.17	(21)
6M HCl	1.16	-	(11)
13M HCl	~ 1.1	0.10	(23)
12.5M HCl, 20% EtOH	0.78	-	(15)
EDTA, 25°C	2.04	-	(17)
<u>Anion Resin Systems</u>			
Thiocyanate, room temp to 87°C	1.09 to 1.20	8.6 (33°C)	(19),(26)
10M LiCl, 0.1M HCl, 87°C	~ 1.2	~ 9	(24)
Lithium nitrate, 22.5°C	1.9	-	(20)
Lithium nitrate, 87°C	1.6	-	(20)
90% MeOH, 10% 1M HNO ₃ , room temp	3.25	-	(2)
7N Al(NO ₃) ₃ , 0.01N HNO ₃ , 40°C	2.2	-	(28)
4.5N Ca(NO ₃) ₂ , room temp?	1.8	-	(28)
6N Mg(NO ₃) ₂ , 0.01N HNO ₃ , room temp?	2.35	-	(28)

Table IV indicates that the prospects of achieving two of the secondary purposes of the survey are not very promising in the simple solvent-acid systems considered. A clean-cut separation of the actinide fraction from fission-product rare earths (predominantly elements lighter than terbium) does not appear likely, although it is still possible that some of the systems could be used to eliminate fission-product yttrium, but this remains to be demonstrated. Separation of the individual heavy rare earths also does not appear to be feasible in the simple systems. (Interestingly enough, the data of Kraak and von der Heyden⁽²⁸⁾ indicate that separation efficiency for the heavy rare earths also drops off rapidly in the concentrated $\text{Mg}(\text{NO}_3)_2$ -anion resin system.)

Several solvent mixtures, however, do have promise for separation of americium and promethium, a fact that may be useful in view of the developing promise of isotopes of these two elements as valuable byproducts of reactor operations. As seen from Table V, the two elements tend to elute very close together in most ion-exchange column systems. Concentrated HCl on a cation-resin column gives an excellent separation, but the highly corrosive nature of the reagent, particularly in the atmospheres of hot-cell containment boxes, is a serious drawback. Thiocyanate with anion resin does well, but thiocyanate polymerizes readily in acid solution and the ion reacts explosively with the H_2O_2 produced by reaction of high levels of radiation on water.⁽²⁴⁾ Ten molar lithium chloride at 87°C on anion resin is effective, but this again is a difficult reagent to handle and presents problems when it is necessary to recover microgram quantities of desired products. Comparison of data taken in two different $\text{Mg}(\text{NO}_3)_2$ concentrations (6N and 7N) by Kraak and von der Heyden⁽²⁸⁾ with anion resin indicates that a good americium-promethium separation may be obtained in that system, but this again involves the use of concentrated salt solutions with their attendant handling difficulties.

Table V indicates two interesting systems for further investigation of the americium-promethium separation, those involving Carbitol acetate and tetrahydrofurfuryl acetate, although, since both are esters, reagent stability problems under irradiation may be important. Hexylene glycol would be another possibility if used with the proper diluent to reduce viscosity.

Figure 1 compares lanthanide and actinide relative elution positions in the α -hydroxyisobutyrate^(14,18) and methyl alcohol-nitric acid^(1,2) systems with several solvents studied in the present survey, based on the data of Table IV. [Estimated elution positions were calculated from the methyl alcohol-nitric acid system data of references (1) and (2).] The excellent americium-curium separations obtained in the mixed solvent elutriant systems can be easily seen, as can the possibilities for americium-promethium separation in Carbitol and tetrahydrofurfuryl acetates as discussed above.

Fig. 1. Relative Lanthanide-Actinide Elution Positions

The thulium distribution data of Table IV are somewhat tentative since the K_D values found were, in general, greater than those of terbium, a result that would not be expected from the data of Faris and Warton. The values are presented primarily to indicate that none of the systems are very promising for separations of the elements between terbium and thulium. (Because of the technique used in measuring the K_D values, a small amount of radioactive impurity in the thulium tracer having a strong affinity for the resin could produce a false high value for the distribution. Gamma-ray spectroscopy performed on the tracer did not reveal such an impurity, but a very small amount of non-Tm¹⁷⁰ radioactivity was demonstrated by an isobutyrate separation on cation resin. Corrections were made in the data of Table IV on the assumption that all of the extraneous radioactivity was lost to the resin.)

Based on studies with lanthanum and ytterbium, Kriss and Sheka⁽²⁷⁾ have concluded that in aqueous nitric solutions above 7 molar, the cerium-group rare earths form anionic complexes while the yttrium-group rare earths remain electrically neutral. The water-nitric acid portion of the elutriants discussed in this report presumably concentrate within the matrices of the anion-resin beads. If it is assumed that the local nitrate ion concentration is effectively above 7 molar in the beads, an explanation is available of the difference in behavior between the light and heavy rare earths observed by Faris and Warton in the methanol-nitric acid system

and by Kraak and von der Heyden in concentrated $\text{Mg}(\text{NO}_3)_2$. On the other hand, Korkisch and Janauer⁽¹⁰⁾ believe that as the molar percentage of alcohol increases in these systems, adsorption of neutral complexes becomes increasingly superimposed on the strict anionic exchange mechanism. In some systems, this last effect could conceivably be more important for thulium than for terbium, thus accounting for the K_D reversal in certain cases, as discussed above.

ACKNOWLEDGMENTS

Thanks are extended to K. A. Orlandini for help in the earlier phases of the batch distribution ratio studies, and to F. R. Lawless for his careful study of the Tm^{170} tracer.

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