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BIDENTATE ORGANOPHOSPHORUS COMPOUNDS AS EXTRACTANTS FROM ACIDIC WASTE SOLUTIONS: A COMPARATIVE AND SYSTEMATIC STUDY*

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SUMMARY

A comparative study has been made of seven bidentate organophosphorus compounds, of the type tetraalkyl carbamoylmethylphosphonate, as extractants for trivalent actinides from strong (6 M HNO_3) acid solutions. Such extractants provide one approach for removing alpha-emitting nuclides from radioactive waste solutions. The compounds dihexyl [(diethylcarbamoyl)methyl]-phosphonate (DHDECMP) and di(2-ethylhexyl) [(diethylcarbamoyl)methyl]phosphonate (DEHDECMP) appear to be the most useful of the carbamoylmethylphosphonates (CMPs) now available. The lower-molecular-weight and normal-alkyl-substituted members of this group of compounds are better actinide extractants, but the higher-molecular-weight compounds have lower aqueous-phase solubilities. The solubility of DHDECMP in water is approximately the same as that of TBP in water, and the solubility of DEHDECMP in water is about 3 % of that of DHDECMP (0.4 mg/liter when a 0.1 M solution of DEHDECMP in cyclohexane is equilibrated with a 1000-fold excess of water). Of the compounds examined, those with branched substituents are more soluble in normal hydrocarbons and more resistant to third-phase formation on contact with nitric acid

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*Research sponsored by Energy Research and Development Administration under contract with the Union Carbide Corporation.

DISCLAIMER

(a third phase consists of the nitric acid adduct of the CMP that separates from the bulk of the organic phase after the CMP solution is contacted with HNO_3). However, these branched compounds appear to be somewhat poorer extractants, possibly due to steric hindrance in formation of the metal adduct. A mixed aliphatic-aromatic diluent is useful to maximize extraction and maintain adequate extractant and adduct solubility. Some commercially available mixed diluents are suitable for use with these compounds. A single-CH_2-group spacing between the coordinating oxygens is optimum for metal adduct formation with the CMPs. The tetraalkyldiphosphonates, which are compounds with structures similar to the CMPs, are less useful extractants than the CMPs due to solubility and viscosity limitations.

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ABSTRACT

A comparative study has been made of several bidentate organophosphorus compounds. Tetraalkyl carbamoylmethylphosphonates and tetraalkylalkyl diphosphonates were tested for their ability to extract americium from nitric acid. Aromatic, aliphatic, and mixed diluents were compared as to the effect on extraction behavior, aqueous-phase solubility, and organic-phase solubility. Reagent and acid dependences are presented for selected compounds.

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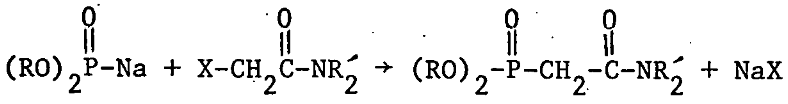
INTRODUCTION

In the early 1960's, Siddall demonstrated that the dialkyl [(dialkylcarbamoyl)methyl]phosphonates would extract trivalent lanthanides and actinides from strong nitric acid solutions.[1,2] He later patented the use of these bidentate compounds for the removal of trivalent americium and curium from highly acid (2-6 M HNO_3) Purex waste streams.[3] These compounds are superior to monodentate extractants, such as tributylphosphate (TBP) or dibutyl butylphosphonate (DBBP), for extraction from such solutions. The monodentate extractants require highly salted solutions at lower acid concentrations.

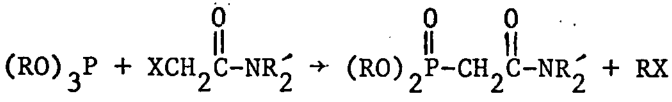
More recently, workers including Schulz at Atlantic Richfield Hanford Company, Richland, Washington, and McIsaac at Allied Chemical Corporation, Idaho Falls, Idaho, have studied the use of organophosphorus bidentate extractants for the removal of alpha-emitting nuclides from acidic radioactive wastes at their respective locations.[4,5] Wastes at both Hanford and Idaho Falls are highly salted. A typical composition can be seen in Table 1. Three extraction cycles of a simulated waste of this type using 30 vol % (0.9 M) dibutyl [(diethylcarbamoyl)methyl]phosphonate (DBDECMP) reduced the plutonium content of the waste by a factor of greater than 5000 and the americium content by a factor of 600.[5] The chemical and radiochemical character of waste varies with the site, depending upon the type of material processed. Since many wastes with which we will be required to deal at ORNL are acid solutions containing minimum amounts of salt, our study of the bidentate extractants has been concerned with obtaining and testing compounds that would extract from acid solutions containing little or no salts with a minimum loss of the reagent to the aqueous phase.

One of the problems associated with the use of the tetraalkyl carbamoylmethylphosphonates is the presence, in most preparations, of some impurity that extracts trivalent actinides at low acidities and retains them when normally used water stripping is attempted. These compounds may be prepared by the Michaelis reaction:



$$(RO)_2\overset{O}{\overset{\|}{P}}\text{-Na} + X\text{-}CH_2\overset{O}{\overset{\|}{C}}\text{-}NR'_2 \rightarrow (RO)_2\text{-}\overset{O}{\overset{\|}{P}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}NR'_2 + NaX$$

or by the Arbuzov rearrangement:



$$(RO)_3P + XCH_2\overset{O}{\overset{\|}{C}}\text{-}NR'_2 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{-}CH_2\overset{O}{\overset{\|}{C}}\text{-}NR'_2 + RX$$

where R and R' are normal or branched chain alkanes and X is chlorine or bromine.[1,2] With the larger, branched R groups of interest, the Arbuzov rearrangement takes place only at temperatures of 200°C or higher and significant product loss is encountered by the formation of impurities requiring removal from the primary product.

One or more of the principal impurities present in the technical-grade tetraalkyl carbamoylmethylphosphonates (CMPs) is believed to be an acidic material since it creates a serious problem in stripping the trivalent actinides from the CMP solution by water or low concentrations of nitric acid. The impurities present in these commercial preparations have been studied by workers at Battelle-Pacific Northwest Laboratory, Rocky Flats, and Oak Ridge National Laboratory.[6,7,8] Methods of studying the impurities have varied. Martin at Battelle examined both technical-grade and purified material by GC-MS, NMR, and IR.[7] Thin layer and column chromatography combined with radiotracer testing, elemental analysis, and IR were used by Bahner at ORNL to investigate an enhanced source of impurities, i.e., the pot residue from molecular distillation of technical-grade CMPs. Martin and Bahner have concluded that the principal offending impurity is alkyl [(dialkylcarbamoyl)methyl]phosphonic acid.[8]

Various methods have been used to purify the technical-grade CMPs. Schulz prepared satisfactorily pure reagent for his applications using Siddall's method of acid hydrolysis and alkaline wash.[4] More recently, at the same installation, purifications have been carried out by washing a dihexyl [(diethylcarbamoyl)methyl]phosphonate (DHDECMP) solution with ethylene glycol and then passing the material through a macroreticular, strong base (Rohm and Haas A-26) ion exchange resin column to remove acidic impurities.[9] Kilogram amounts of CMPs for bench-scale research are purified at ORNL by molecular distillation. McIsaac has recently used a purification consisting of molecular distillation followed by a pass through a silica gel column. Gas chromatographic analysis of this purified material indicates a very pure product.[10]

The choice of a suitable compound for study and use at Idaho Falls was initially DBDECMP.[5] This compound is as good an extractant as DHDECMP and appeared to be more easily purified; however, a significant aqueous-phase solubility hindered its practical use in a continuous solvent extraction system. The choice made by workers at Hanford and Idaho Falls is now DHDECMP. This compound has adequate actinide extraction power and low aqueous-phase solubility (similar to that of TBP in water).

This research is addressed to the problems of selecting and testing bidentate organophosphorus extractants having low aqueous-phase solubility, high organic-phase solubility, and adequate extractant power. We are studying new compounds in which the R groups on the end (or both ends) of the molecule are made larger and/or branched with the objective of decreasing the aqueous-phase solubility and making the compound more compatible with straight-chain aliphatic diluents.

EXPERIMENTAL

The tetraalkyl carbamoylmethylphosphonates were obtained as technical-grade material from the Wateree Chemical Company, Lugoff, South Carolina. They were purified for this study by molecular distillation at a pressure of $\sim 1\ \mu$ and a temperature of 55 to 105°C (depending upon alkyl chain lengths and branching). The distilled products were checked for the absence of acidic extractants by testing their ability to extract americium from 0.01 $\underline{M}$ HNO_3. Elemental analyses of the molecularly distilled compounds were done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Diluents for the extractants were reagent- or commercial-grade quality and used without further purification. Aqueous acid solutions were prepared from reagent-grade concentrated acid.

Radioactive tracers were obtained from ORNL, ICN, or New England Nuclear.

Equilibrations were performed by shaking 5 ml of each phase for at least 15 min in cylindrical separatory funnels equipped with Teflon stopcocks. Previous experiments indicated that equilibrium was reached in <1 min. After phase separation, 1-ml samples of each phase were taken for gamma counting. The distribution coefficient, D, was then calculated from the ratio of the count rate in the organic phase to that in the aqueous phase.

The organic phases containing the extractant were pre-equilibrated twice with acid of the concentration to be used in the experiment to ensure the desired equilibrium concentration of acid during the extraction.

RESULTS AND DISCUSSION

Comparison of Carbamoylmethylphosphonates

Seven compounds were tested using, in each case, molecularly distilled fractions. Elemental analyses of these compounds (Table 2) are in excellent agreement with the theoretical values. In addition, tests of americium extraction at low acid concentrations assured us that the acidic compounds that prevent low acid stripping of americium were not present. Extraction coefficients in the presence of 0.01 M HNO_3 were typically <0.1 for all the purified compounds.

Table 3 shows the comparative capabilities of the seven compounds to extract americium. The effect of reagent structure on extraction can be seen in the results in diethylbenzene (DEB) and dodecane where, in general, the smaller (but more aqueous-soluble) compounds are better extractants. Although more of the compounds are soluble in DEB without third-phase formation (a third phase consists of the nitric acid adduct of the CMP that separates from the bulk of the organic phase after the CMP solution is contacted with HNO_3), distribution coefficients are higher in dodecane. It is clear that the type of diluent, aliphatic or aromatic, as well as the structure of the extractant, is important in determining the extraction behavior of these compounds.

Choice of Diluent

Aliphatic diluents have the advantage of providing a higher americium distribution coefficient than do aromatic diluents; however, if one desires to use an aliphatic diluent, those compounds with straight alkyl chains on either end (e.g., hexyl and ethyl or butyl and ethyl) should be avoided. Such compounds extract nitric acid (about 2 moles of acid per mole of CMP), and the nitric acid adduct separates into a third phase. An aromatic diluent such as DEB successfully circumvents the third-phase problem but depresses distribution coefficients by a factor of 2 or more. An organic-soluble--aqueous-insoluble modifier such as tridecanol (TDA) may also be added to prevent third-phase formation. Fifteen percent by volume (vol %) TDA was necessary to prevent third-phase formation in a 30 vol % (0.8 $\underline{M}$) solution of DHDECMP in dodecane when contacted with 6 $\underline{M}$ HNO_3. The americium distribution coefficient (D_{Am}) in this system is 9.2, as compared with 4.5 in the system with DEB as a diluent. Several diluents were tested with di(2-ethylhexyl) [(diethylcarbamoyl)methyl]phosphonate (DEHDECMP) in the extraction of americium from 6 M HNO_3. These comparisons may be seen in Table 3.

Figure 1 shows the effect of the aliphatic-aromatic content of the diluent on the extraction of americium from 6 M HNO_3 by 0.5 M DEHDECMP. In this test the xylene concentration in dodecane was varied from 100 vol % to 5 vol %. It was possible to obtain extraction data down to 10% xylene; third-phase formation occurred at 7.5% xylene. The D_{Am} increased rapidly until the aromatic content of the mixture dropped to about 15 vol %. These results suggest that an aromatic content of 10 to 15% would be an optimum diluent composition.

The significant effect of the diluent type both on extraction power and solubility prompted a study of two commercial diluents[11] (containing both aromatic and aliphatic components) that are prepared for the solvent extraction industry, KERMAC 470B and KERMAC 627. Comparisons may be seen in Table 3. The effect is apparent for dihexyl [(diisobutylcarbamoyl)methyl]-phosphonate (DHDIBCMP) and DEHDECMP in KERMAC 470B. Neither compound is compatible with dodecane upon contact with 6 M HNO_3; however, each remains in solution at 0.7 M in KERMAC 470B and exhibits an adequate distribution coefficient for americium when used in the mixed diluent.

Systematic Studies of DHDECMP and DEHDECMP

The compounds DEHDECMP and DHDECMP were chosen for more extensive descriptive studies because DHDECMP is being used or planned for use (along with either chlorinated or aromatic diluents) at both Hanford and Idaho Falls and DEHDECMP appears to offer the advantages of lower aqueous-phase distribution of the extractant and higher organic-phase solubility. When used in a mixed aromatic-aliphatic diluent, DEHDECMP has a very low aqueous-phase solubility (about 3% that of DHDECMP) and shows no evidence of third-phase formation upon acid contact up to 8 M HNO_3. At a concentration of 1 M (extracting from 6 M HNO_3), it gives an americium distribution coefficient of 17.5 (see Fig. 2). Equilibration of this organic with fresh 6 M HNO_3 gave an americium distribution coefficient within experimental error, indicating the equilibrium value may be approached from either direction. Some limitations exist in the capacity of this extractant mixture for metal adduct. Attempts to load a 0.5 M DEHDECMP solution in a mixed diluent (KERMAC 470B) with europium from 6 M HNO_3 produced a third phase when the europium concentration was 0.02 M in the aqueous phase.

The dependence of americum extraction on reagent concentration for DHDECMP in DEB is seen in Fig. 3. A least-squares fit of these data indicates that the americium distribution coefficient is proportional to the 3.2 power of the reagent concentration, suggesting that the average number of extractant molecules associated with each americium is about 3. Figure 2 shows that the reagent concentration dependence for DEHDECMP in KERMAC 470B is 2.5 power, suggesting either that the branching on the extractant molecule may be causing some steric hindrance or that polar materials in the mixed diluent may be included in the organic-phase adduct.

Curves illustrating the dependence of americium extraction on acid concentration are shown in Fig. 4. The curve for 30 vol % (0.8 M) DHDECMP in dodecane modified with 15 vol % TDA is somewhat steeper than that for the same concentration of the compound in DEB. For the latter system, the curve forms a straight line up to about 2 M HNO_3 and then decreases in slope to become nearly flat between 4 and 10 M HNO_3. The dependence of americium extraction on acid concentration over the straight portion of each curve is about 1.5 power.

Figure 5 shows the dependence of americium extraction on aqueous acid concentration for DBDECMP in DEB. This dependence appears to be greater than that for the other compounds at lower acidities; however, the curve does not form a straight line, possibly reflecting the significant aqueous-phase solubility of this extractant at the higher acid concentrations.

The dependence of americium extraction on aqueous acid concentration for DEHDECMP at 30 vol % (0.7 M) and 50 vol % (1.1 M) in DEB is shown in Fig. 6 and for 0.5 M DEHDECMP in both KERMAC 470B and KERMAC 627 in Fig. 7. The dependence appears to be less than second power for the extractant in DEB and about second power for the extractant in the mixed diluents in the straight-line portion of these plots. A third phase was formed in the KERMAC 627 in those experiments equilibrated with HNO_3 at concentrations higher then 5 M. This is probably due to the lower aromatic content of KERMAC 627.

Other Elements

As a part of the systematic study, distribution coefficients have been determined for the following elements from 6 M HNO_3 with 0.5 M DEHDECMP in KERMAC 470B as the extractant:

Element	D
Cs	3.3×10^{-4}
Sr	2.6×10^{-3}
Co	2.6×10^{-3}
Ag	7.1×10^{-3}
Eu	2.13
Tm	0.63
Am	3.4

The separation factor between americium and europium (representing the middle lanthanides) is 1.6, while the separation factor between americium and thulium (representing the heavy lanthanides) is 6. Intergroup separation between the actinides and lanthanides would be very difficult with this extractant system, especially with light and middle lanthanides.

Comparison of Tetraalkylalkyldiphosphonates and Tetraalkyl Carbamoylphosphonate

The tetraalkylalkyldiphosphonates are structurally similar to the carbamoylmethylphosphonates. We have examined five diphosphonates and one carbamoylphosphonate. Results of tests for americium extraction from

6 M HNO_3 are shown in Table 4. In the first three compounds, the distance between phosphonate groups was varied from one to three methyl groups. This comparison shows a marked decrease in americium distribution as the distance between the coordinating oxygens is increased. A comparison of two compounds with two-carbon midchains, one having normal and the other having branched end groups, shows that the compound with normal alkyl groups gives an americium distribution coefficient about four times that of the branched compound. This suggests that branching sterically interferes with formation of the metal salt adduct. The di(2-ethylhexyl)-(diethylcarbamoyl)phosphonate (DEHDECP), which differs from the DEHDECMP only in the absence of the mid-CH_2 group, has an americium distribution coefficient under identical conditions of about 13 times less than that for the DEHDECMP. From this and the results of varying the P = 0 spacing in the diphosphonates, it appears that the single-CH_2-group spacing (giving a six-membered ring in the adduct if bidentate bonding occurs) is the optimum structure for this class of compounds.

High viscosity and apparent low loading capacities for the diphosphonates have kept descriptive study of these compounds at a minimum.

CONCLUSIONS

The compounds DHDECMP (presently in use) and DEHDECMP (an attractive alternate) appear to be the most useful of the CMPs presently available. While the lower-molecular-weight and normal-alkyl-substituted members of this group of compounds are more effective actinide extractants, the higher-molecular-weight compounds have lower distribution to the aqueous phase.

Of the latter, the compounds with branched substituents have higher organic-phase solubilities in normal hydrocarbons. A mixed aliphatic-aromatic diluent is useful to maximize extraction and maintain adequate extractant and adduct solubility. Some commercially available mixed diluents are suitable for such applications. A single-CH_2-group spacing between the coordinating groups is optimum for adduct formation. Tetraalkyl-diphosphonates are less useful extractants than tetraalkyl carbamoylmethyl-phosphonates due to solubility and viscosity problems.

Acknowledgment: We would like to express our appreciation to both W. W. Schulz and L. D. McIsaac for samples of two organophosphorus bidentate compounds, and to S. E. Dorris for technical assistance.

NOTATION LIST

CMP = carbamoylmethylphosphonate

D = distribution coefficient (ratio of count rate in organic phase to that in aqueous phase)

D_{Am} = distribution coefficient of americium

DBBP = dibutyl butylphosphonate

DBDBCMP = dibutyl [(dibutylcarbamoyl)methyl phosphonate

DBDECMP = dibutyl [(diethylcarbamoyl)methyl]phosphonate

DEB = diethylbenzene

DEHDECMP = di(2-ethylhexyl) [(diethylcarbamoyl)methyl]phosphonate

DEHDECP = di(2-ethylhexyl) (diethylcarbamoyl) phosphonate

DEHDIBCMP = di(2-ethylhexyl) [(diisobutylcarbamoyl)methyl] phosphonate

DHDECMP = dihexyl [(diethylcarbamoyl)methyl] phosphonate

DHDIBCMP = dihexyl [(diisobutylcarbamoyl)methyl] phosphonate

DIPB = diisopropylbenzene

GC-MS = gas chromatography-mass spectrometry

IR = infrared spectrometry

KERMAC 470B = a commercial mixed diluent

KERMAC 627 = a commercial mixed diluent

MIBK = methylisobutylketone

NMR = nuclear magnetic resonance

PMH = pentamethylheptane

TBEDP = tetrabutylethanediphosphonate

TBMDP = tetrabutylmethanediphosphonate

TBP = tributylphosphate

TBPDP = tetrabutylpropyldiphosphonate

TDA = tridecanol

TEHEDP = tetra(2-ethylhexyl)ethanediphosphonate

TOEDP = tetraoctylethanediphosphonate

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10. McIsaac, L.D., Personal Communication, March 1977.
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Table 1. Typical composition of Hanford and ICPP actinide wastes*

Hanford CAW solution		ICPP first-cycle waste[b]	
Component	Concentration ($\underline{M}$)[a]	Component	Concentration ($\underline{M}$)[a]
NO_3	5.0	F	3.2
H	2.2	NO_3	2.4
Al	0.8	H	1.6
Na	0.5	Al	0.6
F	0.3	Zr	0.5
Fe	0.009	B	0.2
Si	0.002	Hg	0.04
Ca	0.001	CrO_3	0.01
Ce	0.007	Na	0.01
Mg	0.0006	Sn	0.003
Ni	0.0003	Pu	2200[d]
Pu	0.002-0.01[c]	U	∿1000[d]
^{241}Am	0.002-0.01[c]	Am	40[d]
		Np	10[d]

*Data taken from Schulz, Wallace W., and McIssac, Lyle D., Removal of Actinides from Nuclear Solutions with Bidentate Organophosphorus Extractants, ERDA Report AHR-SA-217, Atlantic Richfield Hanford Company, Richland, Washington (August 1975).

[a] Except where noted.

[b] From co-processing of Zr-clad and Al-clad fuels.

[c] Concentration in g/liter.

[d] Concentration in μg/liter.

Table 2. Elemental analyses of molecularly distilled CMPs

Compound[a]	% Carbon[b] Theor.	% Carbon[b] Found	% Hydrogen[b] Theor.	% Hydrogen[b] Found	% Nitrogen[b] Theor.	% Nitrogen[b] Found
DHDECMP	59.50	59.48	10.47	10.51	3.86	3.74
DBDECMP	54.72	54.88	9.77	9.83	4.56	4.51
DEHDIBCMP	65.68	65.81	11.37	11.22	2.95	2.87
DHDIBCMP	63.01	62.96	10.98	11.07	3.34	3.19
DBDBCMP	59.50	59.49	10.47	10.64	3.86	3.86
DEHDECP	62.22	62.30	10.86	11.02	3.46	3.29
DEHDECMP	63.01	63.05	10.98	11.06	3.34	3.21

[a] Extractant Compounds:
DHDECMP = dihexyl [(diethylcarbamoyl)methyl]phosphonate
DBDECMP = dibutyl [(diethylcarbamoyl)methyl]phosphonate
DEHDIBCMP = di(2-ethylhexyl) [(diisobutylcarbamoyl)methyl]phosphonate
DHDIBCMP = dihexyl [(diisobutylcarbamoyl)methyl]phosphonate
DBDBCMP = dibutyl [(dibutylcarbamoyl)methyl]phosphonate
DEHDECP = di(2-ethylhexyl) (diethylcarbamoyl)phosphonate
DEHDECMP = di(2-ethylhexyl) [(diethylcarbamoyl)methyl]phosphonate

[b] Carbon, hydrogen, and nitrogen analyses by Galbraith Laboratories, Knoxville, Tennessee.

Table 3. Extraction of americium from 6 M HNO_3 by carbamoylmethylphosphonates

Compound[a]	Concentration (vol %)	(M)	D_{Am} in indicated diluent						
			KERMAC 470B	KERMAC 627	DEB[b]	Dodecane	PMH[c]	DIBP[d]	MIBK[e]
DHDECMP		0.5	*	*					
	30	0.8	*		4.5	9.2[f]		4.7	
	50	1.3			23				
DBDECMP		0.5	*	*					
	30	0.9	*		6.3	*			
DEHDECMP		0.5	3.3	4.1					
	30	0.7	8.3		1.5	*			
	50	1.1			9.5			11	17
DEHDIBCMP		0.5	0.3	0.4					
	30	0.6	*		0.3	0.7			
	50	1.0				2.7			
DHDIBCMP		0.5	2.0	*					
	30	0.7	5.7		0.6	*	5.7		
DBDBCMP		0.5	*	*	1.0				
	30	0.8				*	*		
DEHDECP		0.5	0.36	0.36	0.82				
	30	0.7				0.67			
	50	1.2				1.0			

*Third-phase formation on contact with 6 M HNO_3.

[a] Extractant compounds:
DHDECMP = dihexyl [(diethylcarbamoyl)methyl]phosphonate
DBDECMP = dibutyl [(diethylcarbamoyl)methyl]phosphonate
DEHDECMP = di(2-ethylhexyl) [(diethylcarbamoyl)methyl]phosphonate
DEHDIBCMP = di(2-ethylhexyl) [(diisobutylcarbamoyl)methyl]phosphonate
DHDIBCMP = dihexyl [(diisobutylcarbamoyl)methyl]phosphonate
DBDBCMP = dibutyl [(dibutylcarbamoyl)methyl]phosphonate
DEHDECP = di(2-ethylhexyl) (diethylcarbamoyl)phosphonate

[b] DEB = diethylbenzene

[c] PMH = pentamethylheptane

[d] DIBP = diisopropylbenzene

[e] MIBK = methylisobutylketone

[f] With 15 vol % tridecanol added. Third phase in unmodified dodecane.

Table 4. Extraction of americium from 6 M HNO_3 by diphosphonates

Compound[a]	Concentration (M)	D_{Am} in indicated diluent		
		DEB[b]	50 vol % DEB; 50 vol % dodecane	Dodecane
TBMDP	0.75	4.6	6.8	*
TBEDP	0.5	0.17		*
TBPDP	0.5	0.05		*
TEHEDP	0.5			0.12
TOEDP	0.5			0.46

*Third-phase formation on contact with 6 M HNO_3.

[a] Extractant compounds:
TBMDP = tetrabutylmethanediphosphonate
TBEDP = tetrabutylethanediphosphonate
TBPDP = tetrabutylpropanediphosphonate
TEHEDP = tetra(2-ethylhexyl)ethanediphosphonate
TOEDP = tetraoctylethanediphosphonate

[b] DEB = diethylbenzene.

FIGURE CAPTIONS

Fig. 1. Optimization of americium extraction by variation of the xylene concentration in dodecane.

ORNL DWG 77-682

Fig. 2. Americium extraction dependence on reagent concentration for the system 6 M HNO_3 vs DEHDECMP in KERMAC 470B.

ORNL DWG 77-681

Fig. 3. Americium extraction dependence on reagent concentration for the system 6 M HNO_3 vs DHDECMP in DEB.

ORNL DWG 77-691

Fig. 4. Americium extraction dependence on nitric acid concentration for the systems 0.1 - 10 M HNO_3 vs 30 vol % (0.8 M) DHDECMP, in 15 vol % TDA---dodecane, and 30 vol % (0.8 M) DHDECMP in DEB.

ORNL DWG 77-690

Fig. 5. Americium extraction dependence on nitric acid concentration for the system 1 - 10 M HNO_3 vs 30 vol % (0.9 M) DBDECMP in DEB.

ORNL DWG 77-694

Fig. 6. Americium extraction dependence on nitric acid concentration for the systems 0.1 - 10 M HNO_3 vs 50 vol % (1.1 M) and 30 vol % (0.7 M) DEHDECMP in DEB.

ORNL DWG 77-693

Fig. 7. Americium extraction dependence on nitric acid concentration for the systems 0.01 - 7.5 M HNO_3 vs 0.5 M DEHDECMP in KERMAC 627 and KERMAC 470B.

ORNL DWG 77-692

ORNL DWG 77-682

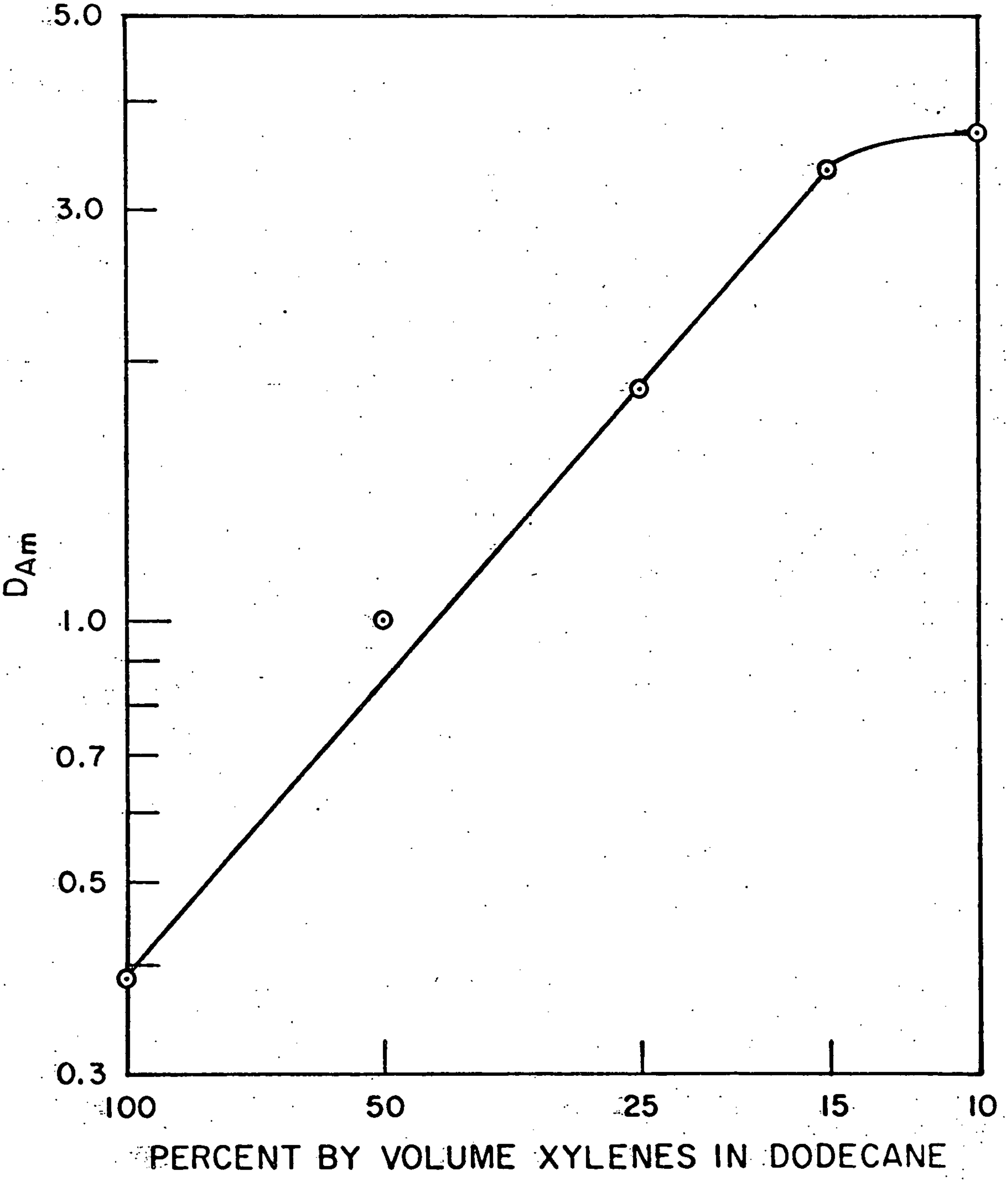

Fig. 1

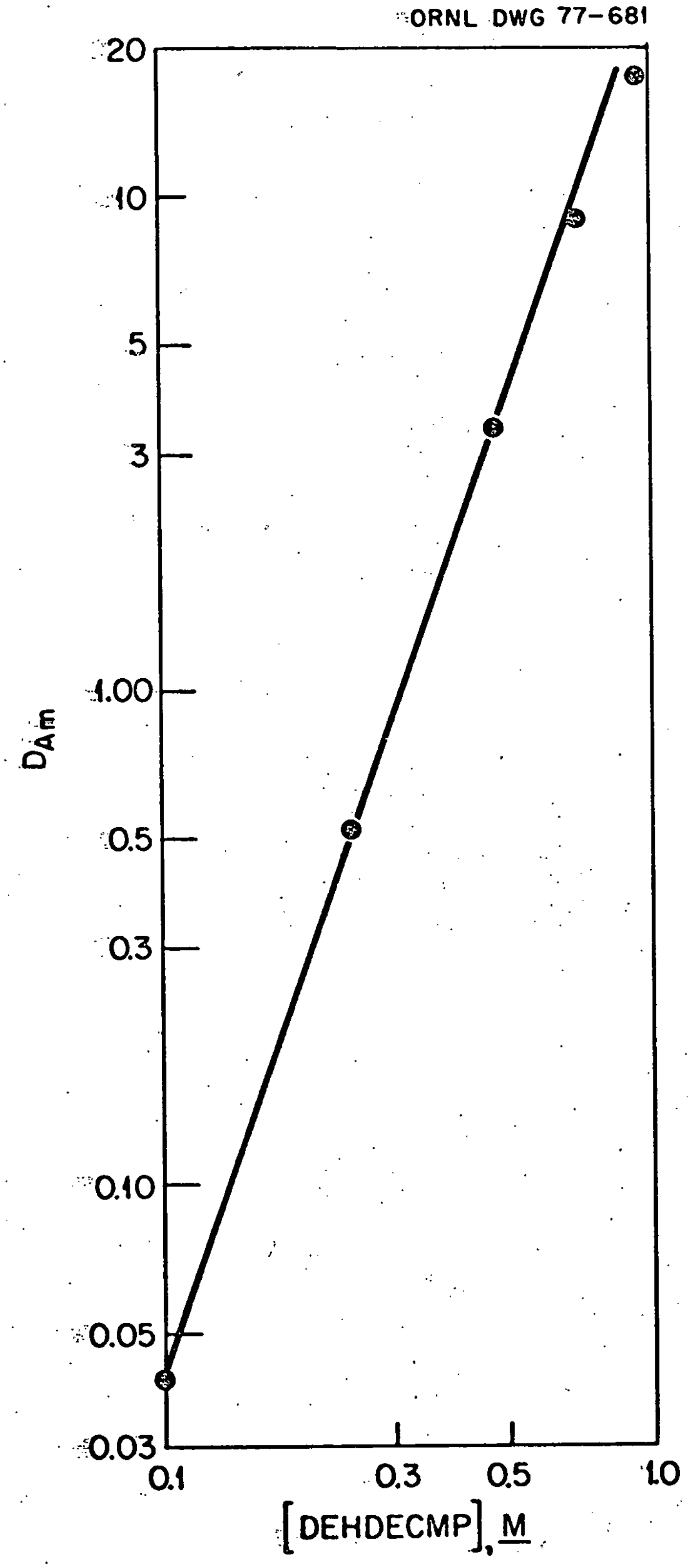
ORNL DWG 77-681
20
10
5
3
1.00
0.5
0.3
0.10
0.05
0.03
D_{Am}
0.1
0.3
0.5
1.0
[DEHDECMP], M

Fig 2

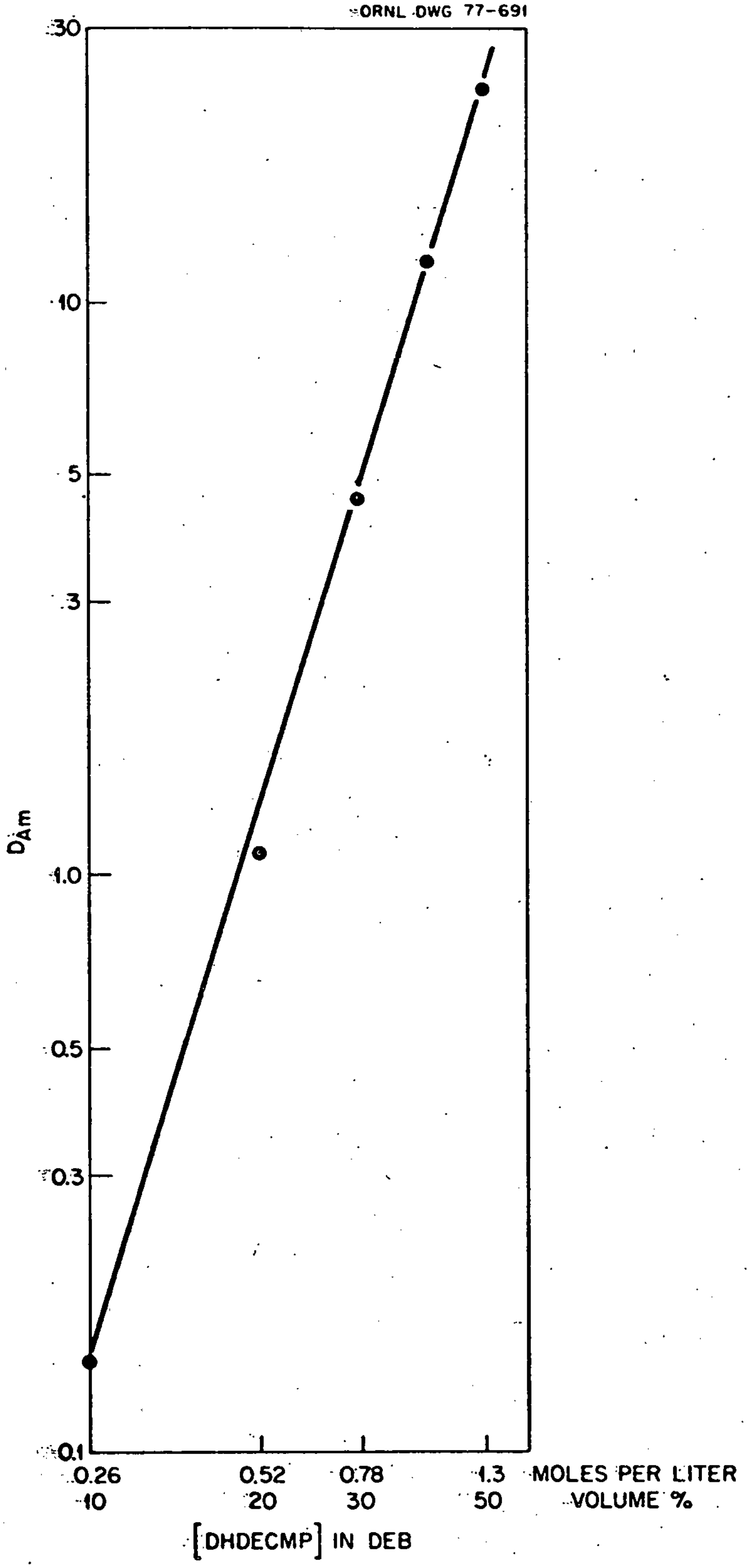
ORNL DWG 77-691
30
10
5
3
1.0
0.5
0.3
0.1
D_{Am}
0.26
10
0.52
20
0.78
30
1.3
50
MOLES PER LITER
VOLUME %
[DHDECMP] IN DEB

Fig. 3

ORNL DWG 77-690

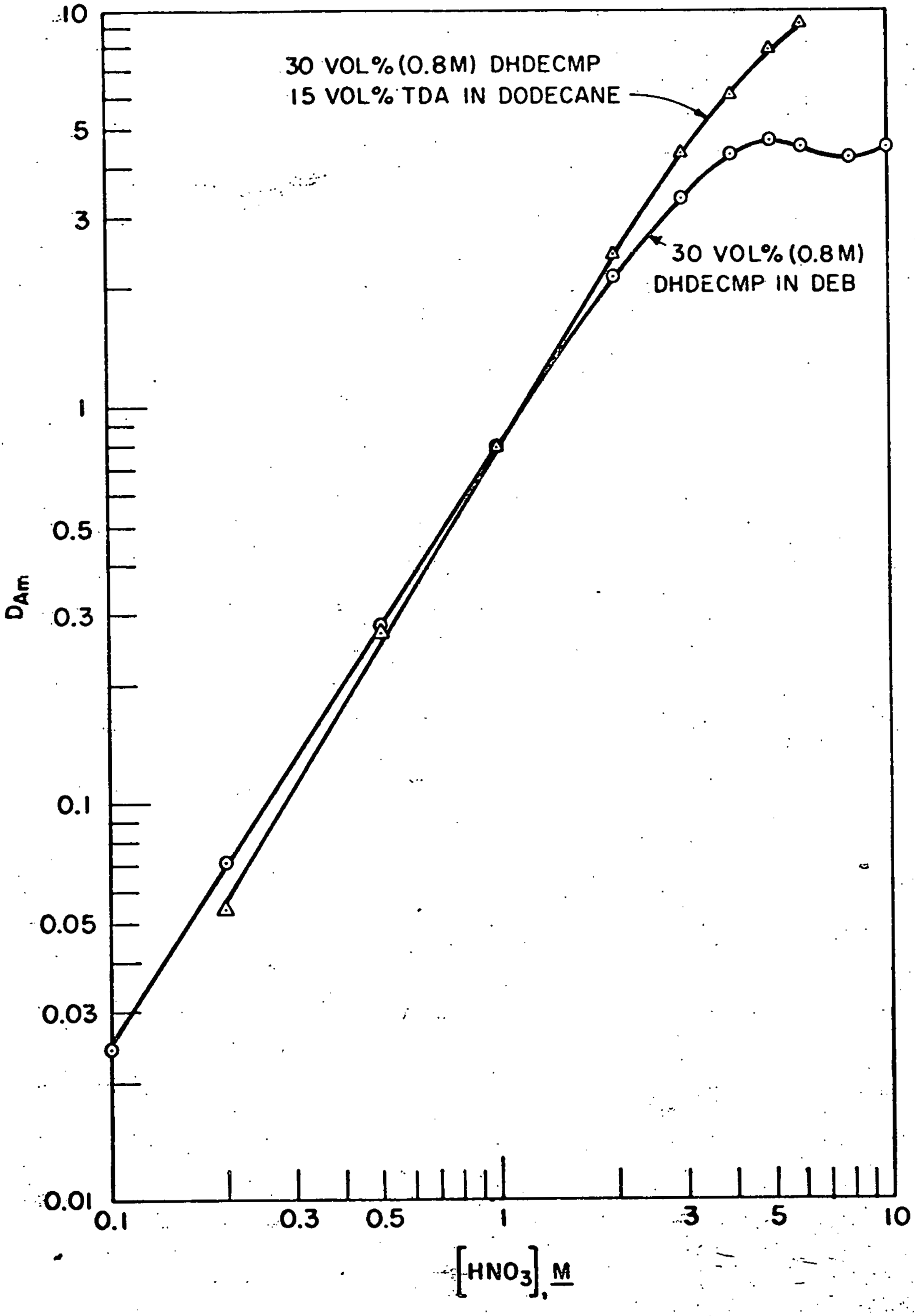

Fig 4

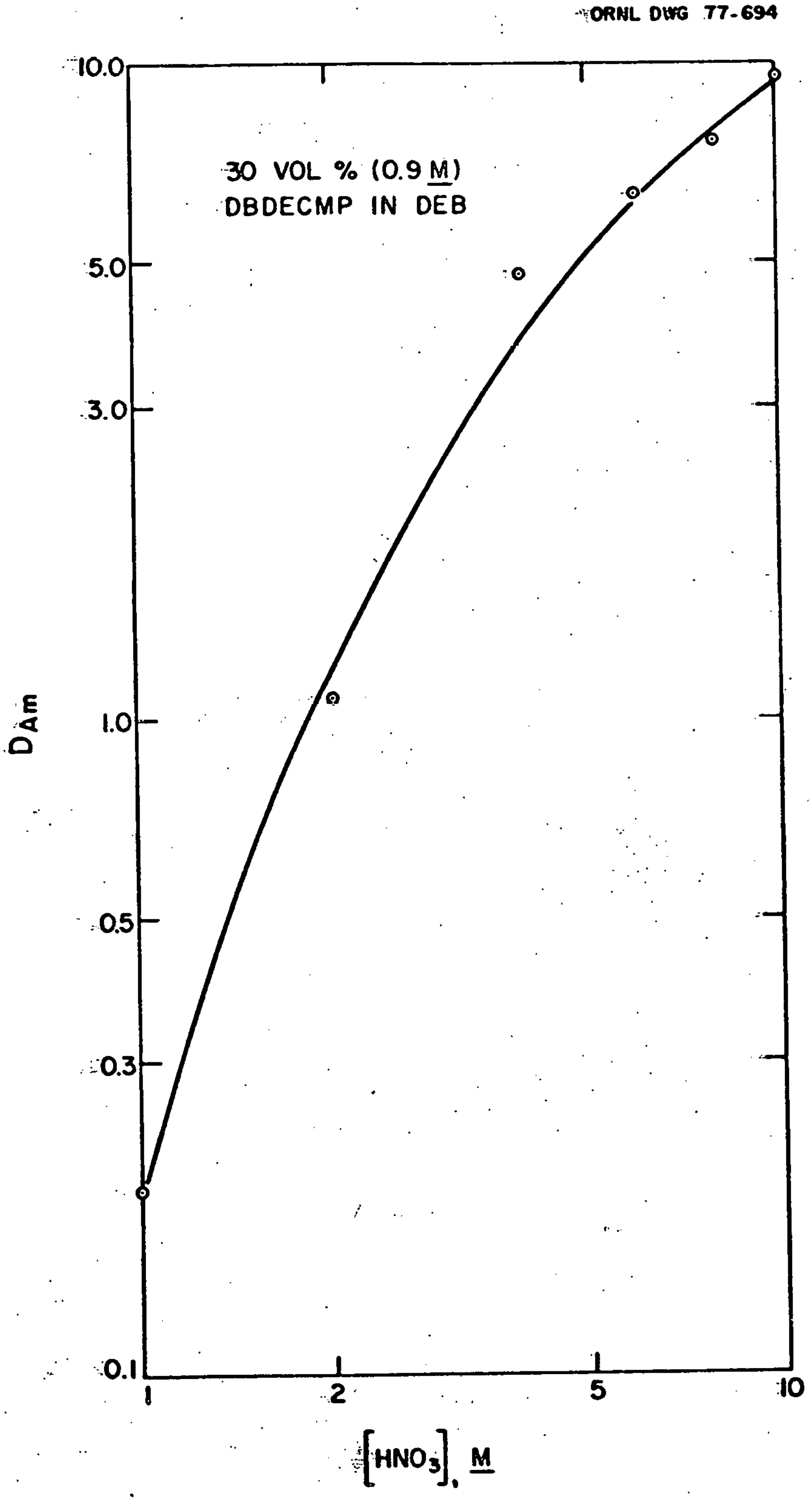
ORNL DWG 77-694
30 VOL % (0.9 M)
DBDECMP IN DEB
10.0
5.0
3.0
1.0
0.5
0.3
0.1
D_{Am}
1
2
5
10
[HNO$_3$], M

Fig. 5

ORNL-DWG 77-693

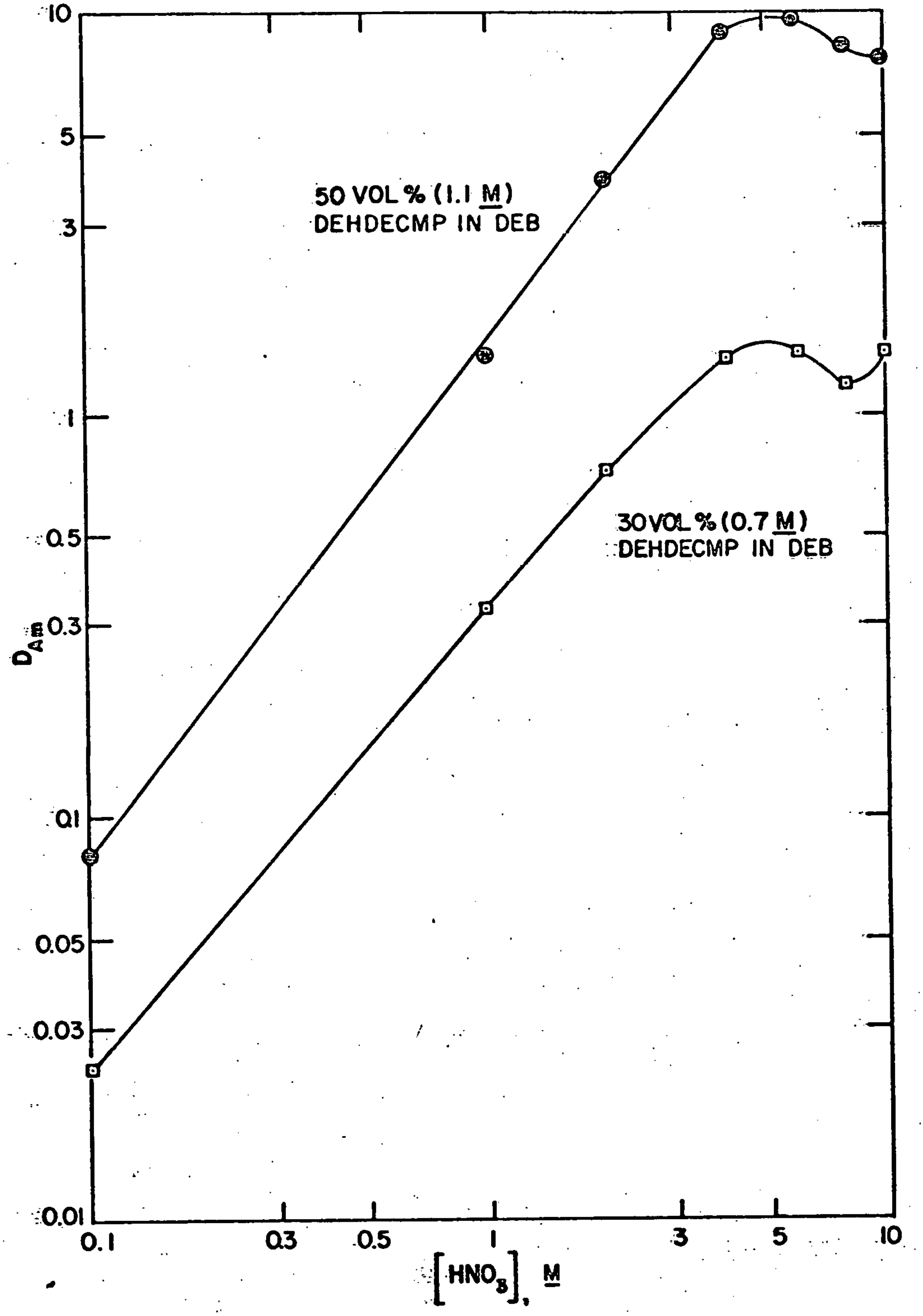

Fig. 6

ORNL-DWG 77-692

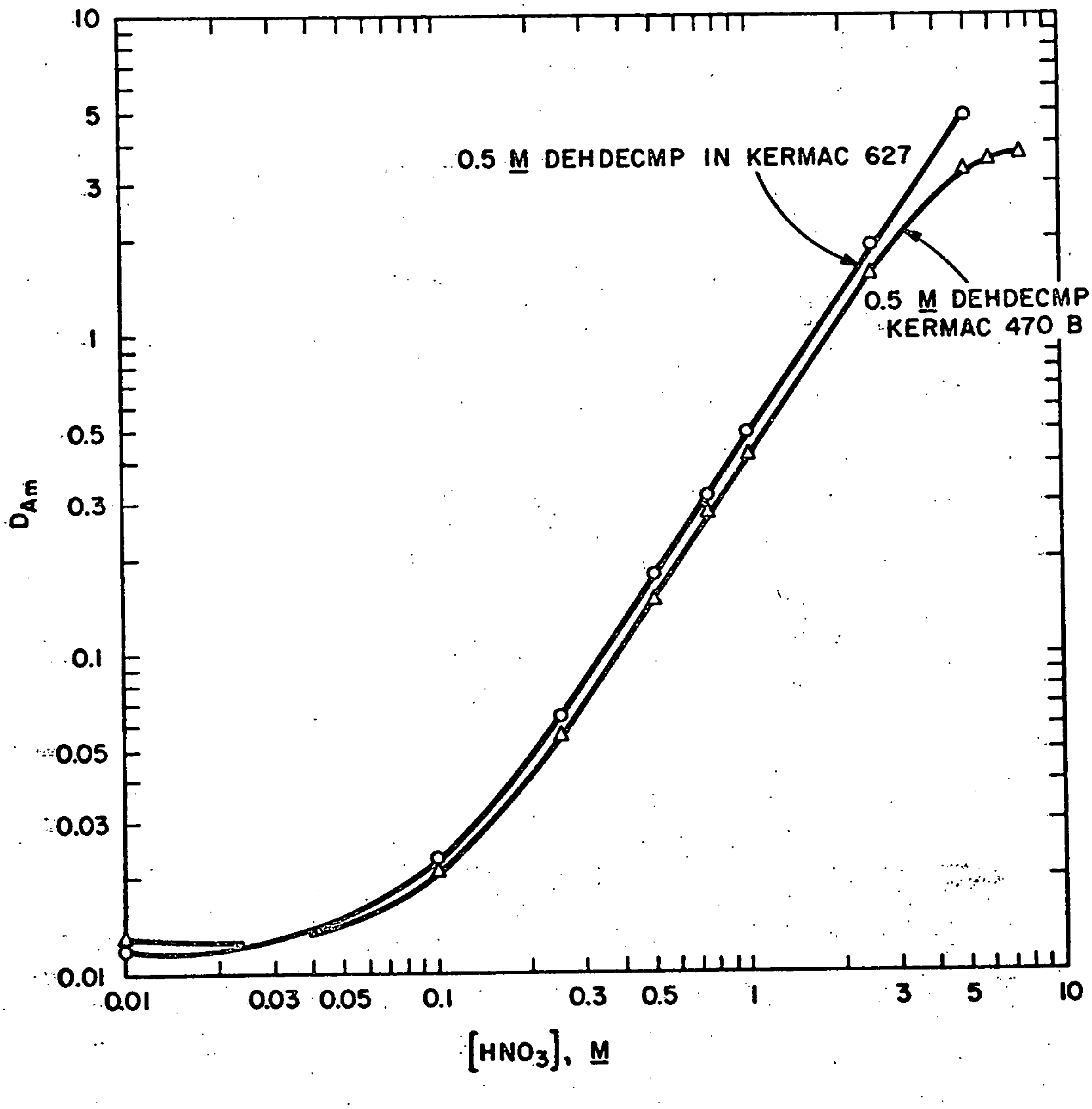

Fig. 7