

ACTINIDE EXTRACTANTS FOR THE NUCLEAR INDUSTRY OF THE FUTURE

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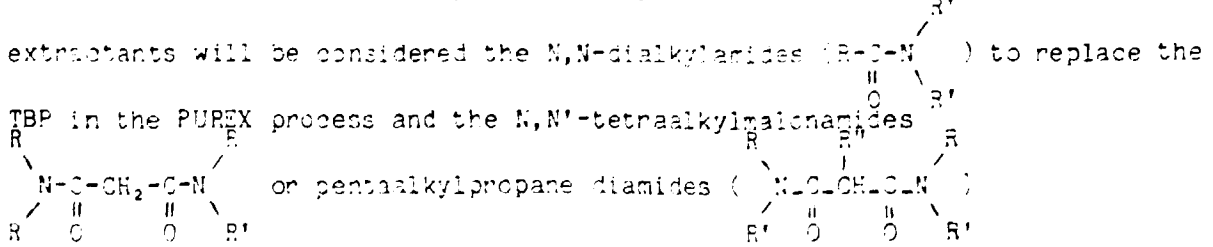
Non organo-phosphorus extractants properties regarding the extractions of actinides in nuclear fuels reprocessing are presented. N,N-dialkylamides are proposed as alternatives to TBP. N,N'-tetraalkylamides or pentaalkyl propane diamides properties are reported. They show that those bidentate extractants are alternatives to bidentate organophosphorus extractants for actinides (III) extraction from concentrated nitric acid.

I. INTRODUCTION

To-day there is no alternative to the PUREX process for irradiated nuclear fuels reprocessing. However if reprocessing has to be applied to all existing fuels it is interesting to look for improvements in the process chemistry in order to simplify it and decrease the cost per kg of reprocessed fuel.

This paper deals with the prospects offered by carboxylic acid amides as alternative extractants to organophosphorus molecules for actinides extraction.

Carboxylic acid amides are completely incinerable and potentially they allow the design of processes producing smaller amounts of radioactive wastes. Monocarboxylic amides main degradation products, carboxylic acid and secondary amine do not affect the separations as does HDBP in the PUREX process. Distinctive properties of amides like the rigidity of the O=C-N bond could be exploited to improve the separation coefficients. Two classes of



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which are species able to extract all the actinides ions, including trivalent, from aqueous acidic nitrate solutions.

II. N,N-DIALKYLAMIDES AS ACTINIDES EXTRACTANTS

N,N'-dialkylamides have been proposed as an alternative to TBP for nuclear fuels reprocessing by several authors (1 to 5). Like TBP they extract selectively U(VI), Pu (IV) from the irradiated fuels nitric, dissolution liquors. They present certain advantages over TBP which can be summarized as follow :

- complete incinerability
- degradation products (carboxylic acid and secondary amine) which do not alter the process, especially there is no formation of insoluble salts ~~like~~ Pu(DBP), Zr(DBP),...
- possibility of higher fission products decontamination factors.
- easier U(VI) back extraction
- better phases disengagement.

However these advantages were partially set aside by the insufficient solubility of nitrate-uranyl amide complexes in the hydrocarbon diluents (2, 3, 4).

Our investigations start with the selection of N,N-dialkylamides suitable for the extraction of macroamounts of U(VI) (80 to 100 g.l⁻¹ of U(VI) in the organic phase), into aliphatic diluents. Selected results are contained in Table I.

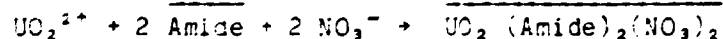
It can be seen that the nature of the alkyl chains is important for precipitation or third phase formation in hyfrane (mixture of C₁₀ to C₁₃ hydrocarbons). The ethyl substitutions in β position from the nitrogen are favorable for the solubility. So our further investigations have been carried out with amide derived from the N,N-di(2-ethylhexyl)amine HN(CH₂-CH-C₂H₅)₂.

C₂H₅

II.1 Extraction of metals

II.1.1. Uranium (VI) : U(VI) distribution ratios between 0.5M DOHA or DOTA into hyfrane and aqueous solutions as a function of aqueous nitric acid concentrations are plotted figure 1.

The extraction mechanism of U(VI) into amidic solvents has been reported (6, 7) previously as :



However we demonstrated that such simple mechanism does not correspond to the reality (8). In addition to the neutral complex mechanism, ion pair formation is involved as it can be seen on figure 2 spectra. The trinitrato species UO₂(NO₃)₃, H(Amide) becomes predominant at high acidities. Distribution ratios of U(VI) as a function of the organic amide concentration are shown figure 3. At low acidities, the slope value (2.35) of the bilogarithmic transform of the extraction curve indicates that the uranyl organic complex contains some amide molecules in its second coordination sphere. Its formula being,

obtained for saturated U(VI) organic solutions in agreement with other authors (7, 9).

II.1.2. Plutonium (IV) : Distribution coefficients of Pu (IV) between 0.5M DOHA or DOTA as a function of aqueous nitric acid concentration are plotted in figure 4. The distribution coefficient of Pu(IV) and U(VI) are compared in figure 5. It can be seen that the U(VI)/Pu(IV) separation factors are higher with DOTA showing the effects of the substituted carbon in β position to C=O. Such features have been reported previously by other authors (1, 4).

II.1.3. Fission products extraction : Distribution coefficients of important fission products between 1M DOHA or 1M DOTA as a function of aqueous nitric acid concentration are plotted in figure 6. It appears that the two oxides yield good U(VI) + Pu(IV)/fission products separation factors. DOTA is ten time more efficient for U(VI)/Zr(IV) separation. Here again it turned out that the substitution favours the separation because its hindering effect is more important for the tetravalent ions.

II.2. Counter current test of DOHA in mixer settler

A counter current test of DOHA for a first cycle of irradiated nuclear fuels cycle has been carried out in laboratory mixer-settlers. The flow sheet diagram is shown in figure 7. The flow-sheet was designed to avoid the U(VI) -Pu(IV) reductive partition. The main results of this test are contained in Table II. For a first attempt, they are encouraging.

Efficiency of the extraction battery was satisfactory, in spite of the high temperature, 41°C at which this run was carried out. It must be remembered that U(VI) distribution ratios decrease with the temperature. The partition in the second battery, was not quite complete and did not verify the flow sheet calculations. Pu(IV) distribution coefficients measured afterwards with the mixer settler solutions indicated that for the used conditions the efficiency of each stage was 0.75. This rather poor efficiency is due probably to slow Pu(IV) back extraction together with too high fluids flow rates. The U(VI) back extraction was complete at room temperature. In this battery rather low stage efficiency was also observed. Nevertheless the chemical factors (low $D_{U(VI)}$ distribution ratios) were so favourable that a U(VI) concentration was made at U(VI) back-extraction. Some Pu(IV) remain in the solvent, probably because of the low acidity used for U(VI) stripping.

II.3. Hydrolysis and radiolysis of DOHA

Chemical and radiochemical stabilities of DOHA have been investigated. For the two types of degradation we followed the concentration of DOHA, hexanoic acid and NN-di(2-ethylhexyl)amine as a function of time. Experiments have been carried out at two nitric acidities 4 and 0.5N. They correspond to two steps of the reprocessing first cycle : the Pu(IV)-U(VI) coextraction and the Pu(IV)-U(VI) partition. The results of hydrolysis are summarized in Table III. They are compared to TBP hydrolysis calculated from the data of Nowak (10). Results of radiolysis are illustrated by the curves of figure 8 which show the % of initial DOHA contained in the irradiated samples. Irradiations were carried out in the presence of nitric acid. Aqueous and organic phases were mixed twice a day. It can be seen that radiolysis yield depends strongly

... of N,N-di(2-ethylhexyl)amine were not successful, probably because the secondary amine produced by hydrolysis or radiolysis degraded faster than it forms. This is not the case for hexanoic acid of which concentrations correspond roughly to the missing DOHA. The comparison of the radiochemical stability of TBP and DOHA is contained in Table IV.

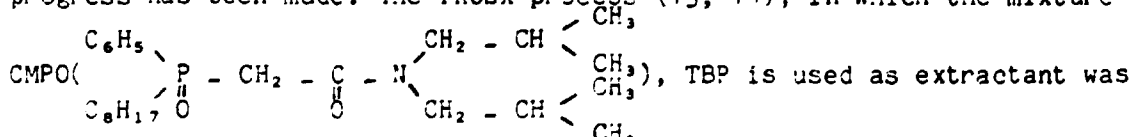
II.4. Future developments for monoamides

The selection of one peculiar monoamide as the best alternative to TBP is probably not possible at the present time. Economic reasons must play an important role in the selection. It is urgent to point out the most important factors which are :

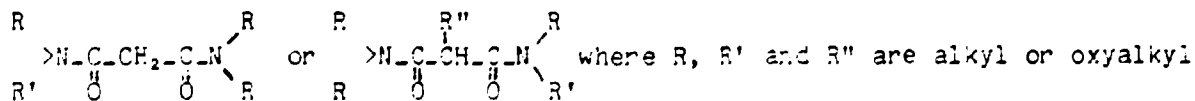
- simplification of the solvent regeneration- ~~process~~
- suppression of the reductive partition
- selectivity regarding the fission products
- cost of the solvent.....

III. SEPARATION OF HIGHLY RADIOACTIVE WASTES ACTINIDES BY TETRA OR PENTAALKYLPROPANEDIAMIDE.

The problem of actinide separation from the highly radioactive wastes has been discussed in many instances. Actinides separations has been recommended from the safety point of view (12). Unfortunately the chemical processes of separation known to day are complicated and unreliable. Improvements are highly desirable. During the last five years, considerable progress has been made. The TRUEX process (13, 14), in which the mixture



designed to remove the actinides from radioactive wastes, in order to avoid their deep underground storage. In spite of the high cost of CMPO and the waste problem associated with this new organophosphorus molecule, the TRUEX process is economically advantageous. At Fontenay-Aux-Roses we investigated the extractive properties of tetraalkyles or pentaalkyles propane diamides with the generic formulae :



radicals.

III.1 Selection of tetra and pentaalkylpropane diamides.

Sidall (15) attempted to extract trivalent actinides and lanthanides by N,N-tetrabutylmalonamide, N,N-tetrabutylloxalamide and N,N-tetrabutylsuccinamide. The poor extraction observed led to the conclusion that diamides were not good extractants for the f series trivalent ions. In order to gain insight into the alkyl group influence upon Am(III) extraction we collected the data contained in Table V.

Distribution ratios are sufficient. Distribution coefficients of Am(III) and Eu(III) as a function of aqueous HNO₃ are plotted in figure 9. Further improvement of Am(III) and Eu(III) extraction were obtained by adding an alkyl group on the central methylene (see figure 10). Distribution coefficients of U(VI)-Zr(IV)-Pu(IV) are plotted in figure 11 as a function of aqueous nitric acid concentration. As for the organophosphorus bidentate extractants Zr(IV) is well extracted and will follow the actinides in real processes so it is necessary to complex it in the aqueous solutions. Oxalic acid is very efficient to hinder Zr(IV) extraction. So it appears that tetra or pentaalkyle propane diamides are promising extractants for actinide separations from concentrated aqueous nitric acid.

III.2. Conclusion

At the present time the pentaalkylpropane diamides look interesting to replace CMPO or other organophosphorus molecules for actinide extraction from nitric acid solutions. Completely incinerable they are not a new source of high volume radioactive wastes. Their cost could be reasonable because of the easiness of preparation and purification. U(VI) and Pu(IV) can be back extracted without chemical transformation, like complexation or change in oxidation state as it is necessary when CMPO is employed. It is obvious that their disadvantage is the large amount of research and development still needed for the confirmation of their usefulness to solve the waste problems. One important point is their stability to radiolysis and the influence of the radiolytic products over the distribution ratios.

IV. GENERAL CONCLUSION

The radioactive waste management become an important part of the nuclear industry. For the wet processes of chemical separations it is possible to limit the amounts of waste by carefully choosing the extractants. Amides are a good alternative to organophosphorus molecules because of their complete incinerability. The donor property of N-C=O group is comparable to the -O-P=O group so actinides are generally better extracted than the fission products. Selectivities difficult to obtain with organophosphorus molecules can be researched by changing the radicals around the amide function. Because of its rigidity, the nature of the radicals influences strongly the steric hindrance.

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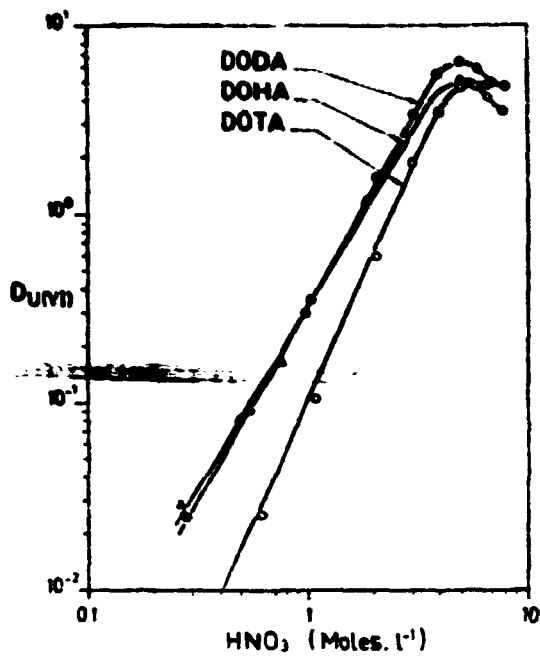


Fig. 1 : $D_{U(VI)}$ vs aqueous C_{HNO_3} (Amide 0.5M into hyfrane)

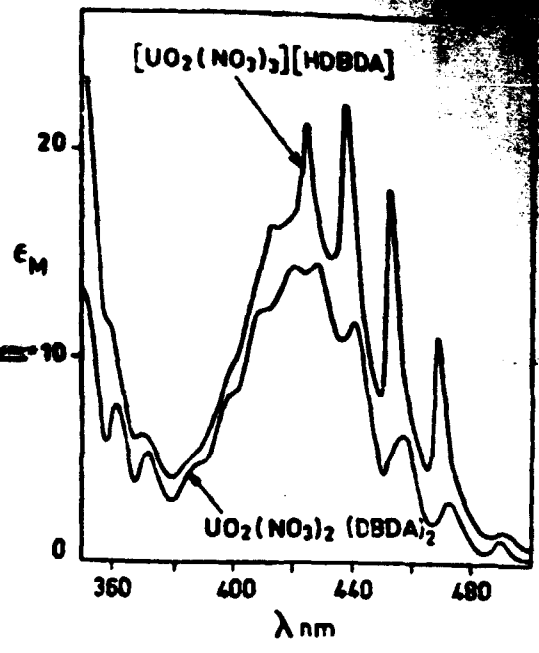


Fig. 2 : U-V-visible organic U(VI) spectra (Amide 0.5M into t-butylbenzene) aqueous acidity 1 and 9N

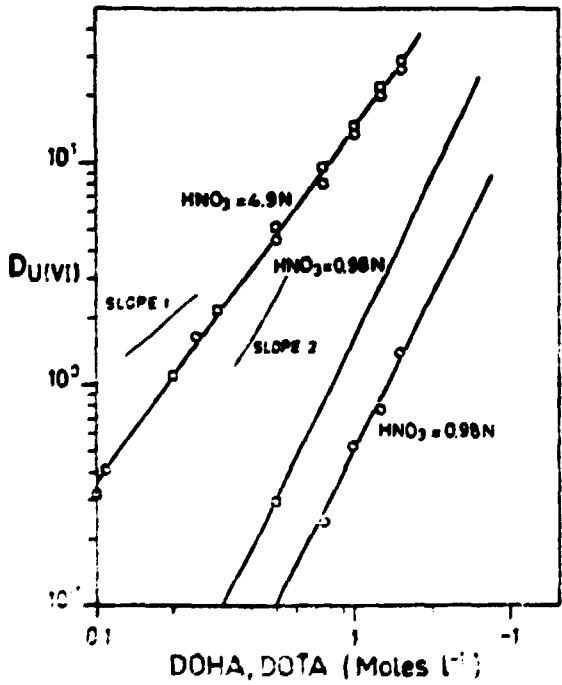


Fig. 3 : $D_{U(VI)}$ vs C_{DOHA} or C_{DOTA}

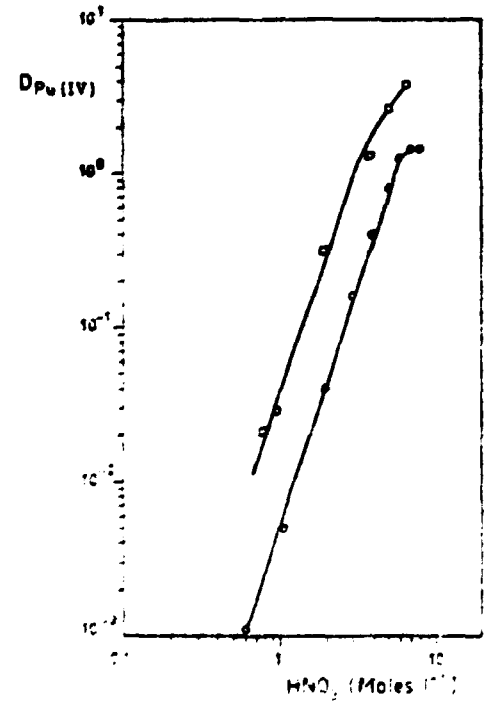


Fig. 4 : $D_{Pu(IV)}$ vs aqueous C_{HNO_3} (DOHA \square , DOTA \circ 0.5M into hyfrane)

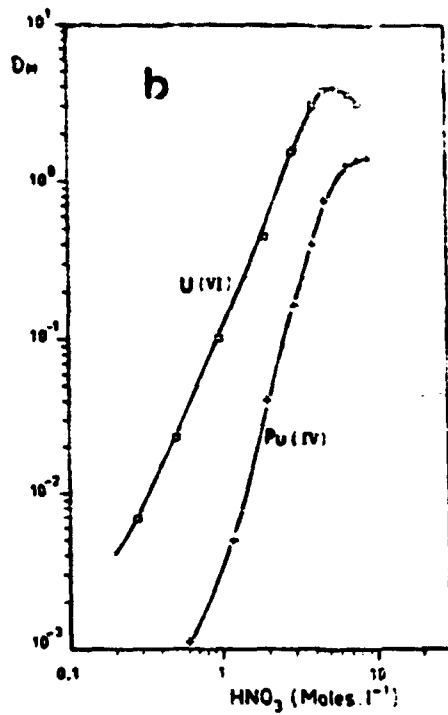
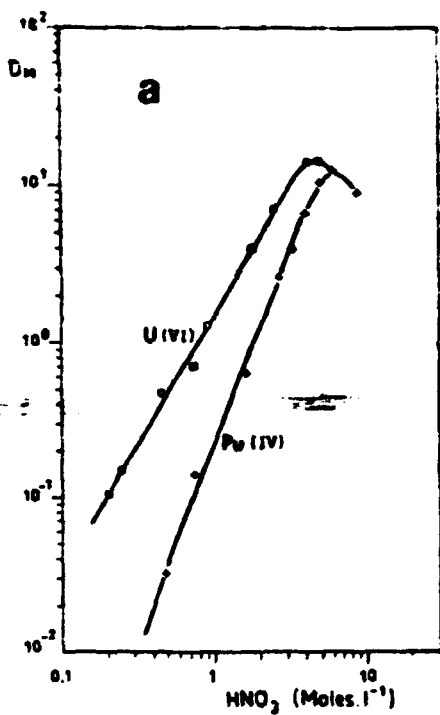


Fig.5 : Comparison of $D_{U(VI)}$, $D_{Pu(IV)}$ vs aqueous C_{HNO_3} a) 1M DOHA b) 1M DOTA)-diluent nyfrane

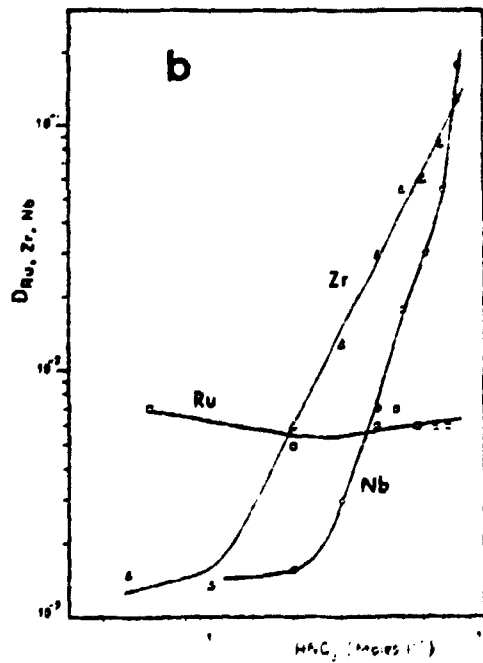
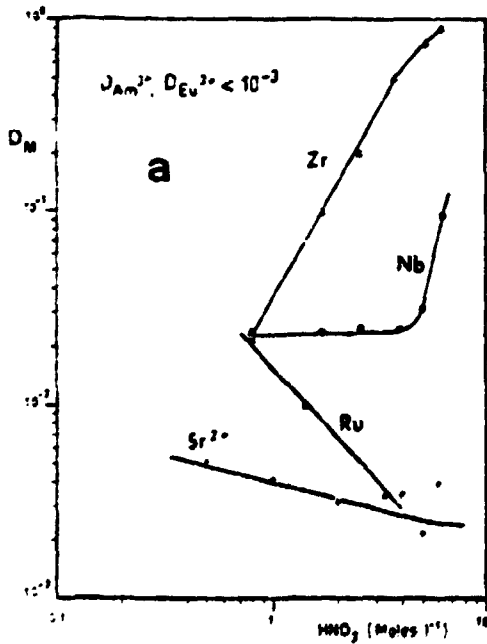


Fig.6 : Distribution ratios of fission products between 1M DOHA (a) or 1M DOTA (b) vs aqueous C_{HNO_3}

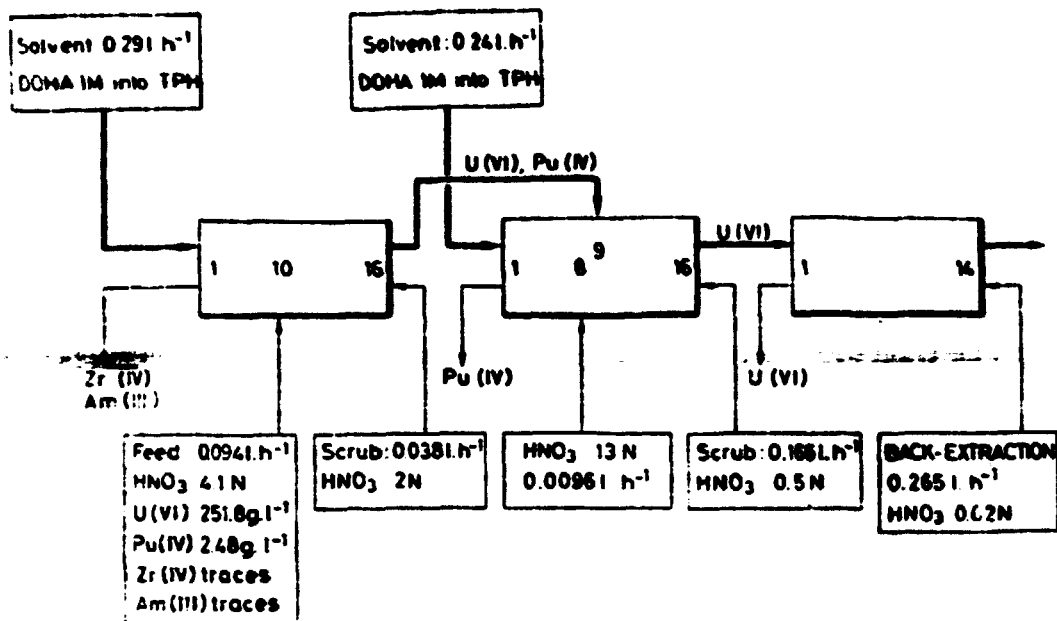


Fig.7 : Flow sheet for a first reprocessing cycle using 1M DOHA into TPH as solvent. No reductive partition.

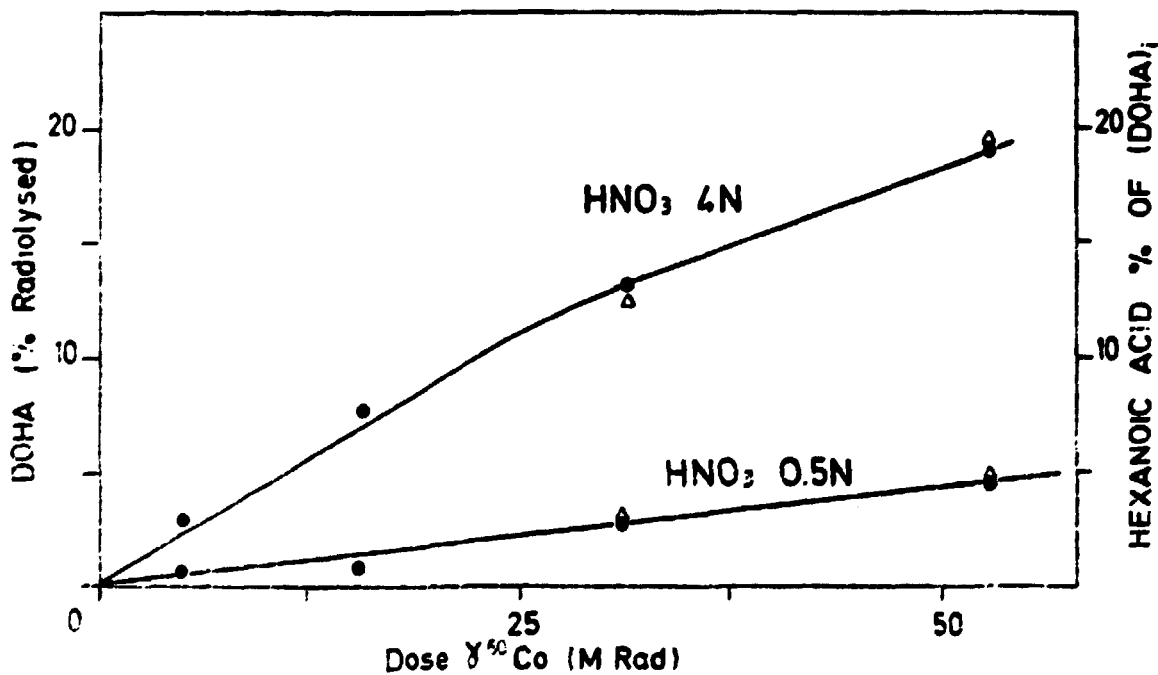


Fig.8 : % of DOHA radiolysed or % of hexanoic acid yields vs irradiation dose (1M DOHA into TPH- $\theta = 40^\circ\text{C}$).

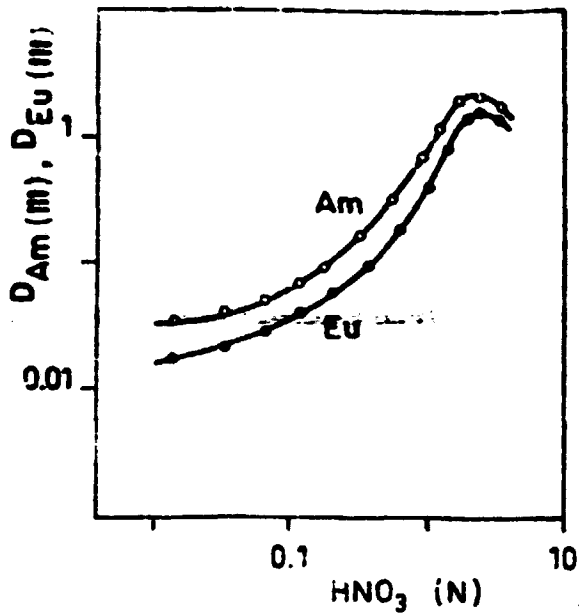


Fig. 9 : $D_{Am(III)}$, $D_{Eu(III)}$ vs aqueous C_{HNO_3} (DMDOMA 1M into t-butylbenzene).

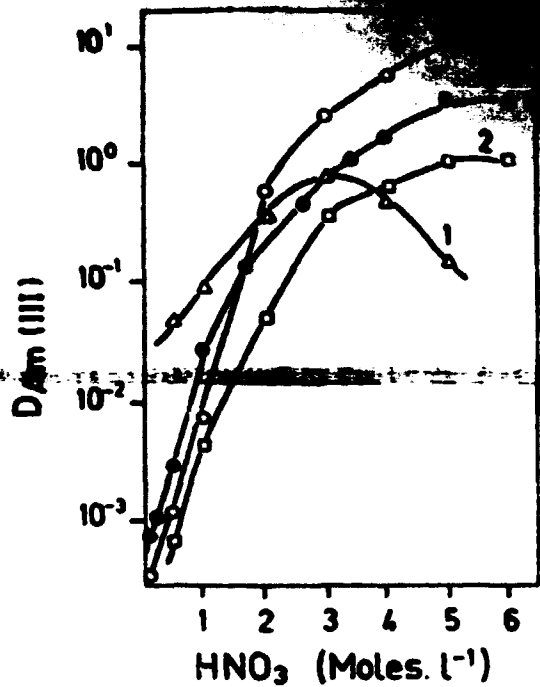


Fig. 10 : $D_{Am(III)}$ vs aqueous C_{HNO_3} (malonamides 0.5M into t-butylbenzene).
 1: $(C_8H_{17}CH_3NCO)_2CH_2$, 2: $(C_4H_9CH_3NCO)_2$,
 3: $(C_4H_9CH_3NCO)_2CH C_2H_4OC_2H_5$, 4: $(C_4H_9CH_3NCO)_2CH C_2H_4OC_2H_4OC_6H_{13}$

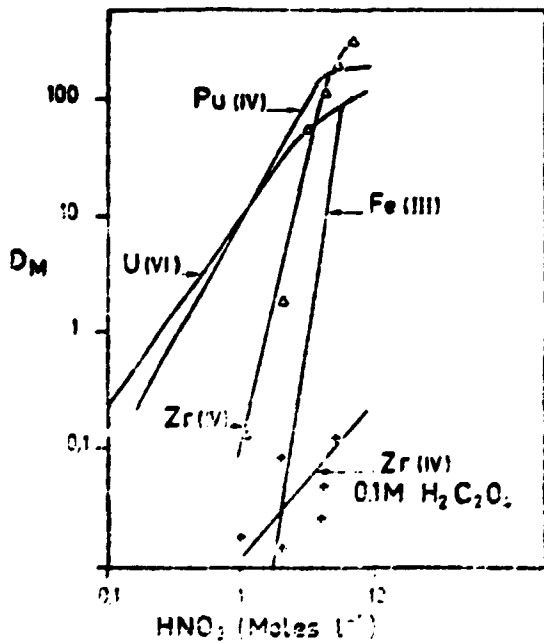


Fig. 11 : D_M vs aqueous C_{HNO_3} ($0.5M(C_4H_9CH_3CO)_2CH C_2H_4OC_2H_4OC_6H_{13}$ into t-butylbenzene).