

UPTAKE OF METAL IONS BY A NEW CHELATING ION EXCHANGE RESIN.
PART 9: SILICA GRAFTED DIPHOSPHONIC ACID*

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ABSTRACT

A new chelating ion exchange resin, Diphonix[®], containing geminally substituted diphosphonic acid ligands bonded to a styrene-based polymeric matrix, was recently developed and characterized. To overcome some of the problems associated with the stripping of actinide elements from the resin, a new version of the Diphonix resin has been prepared, where the chelating diphosphonic acid groups are grafted to a silica support. The new material is called Diphosil, for Diphonix on silica. The properties of the new material have been investigated with regard to its equilibrium and kinetic behavior in the uptake of actinide and other ions from acidic solutions. In this work data comparing the Diphonix and Diphosil resins are presented and discussed. The Diphosil resin appears particularly well suited for those cases where the recovery and further processing of the sorbed actinides is not required and the loaded resin can be considered as a solid waste. Because about 90 % of the Diphosil resin weight is silica, the problem of possible generation of gaseous compounds due to the slow radiolytical degradation of the organic components of the resin is minimized.

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INTRODUCTION

A new chelating ion exchange resin, Diphonix[®], containing geminally substituted diphosphonic acid ligands bonded to a styrene-based polymeric matrix, was recently developed and characterized (1-8). Diphonix also contains the strongly hydrophilic sulfonic acid group in the same polymeric network together with the diphosphonic acid group, in order to provide the polymer with the required high hydrophilicity for fast kinetics of metal species uptake (4).

The most noteworthy property of Diphonix is its extraordinarily strong affinity for actinides, especially in the tetra- and hexavalent oxidation states. The high affinity for actinides, together with the relatively high acidity of the gem-diphosphonic acid group, make possible the sorption of actinides by Diphonix from very acidic solutions. This behavior has been attributed in (1) to the capacity of the resin to chelate actinides through either ionized or neutral diphosphonic acid ligands, leading to metal complexes of high stability.

Because of the high affinity for actinides even when the metal species are present in highly acidic solutions, the Diphonix resin has found application in mixed waste treatment (9) and in analytical procedures for separation and determination of actinides in soil and bioassay samples (10).

The actinides are so strongly retained by the resin that the only effective stripping agents are compounds belonging to the family of aqueous soluble diphosphonic acids, which contain the same ligand group as the resin. Some data on the stripping of actinide species from the Diphonix resin by solutions of the 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) have been reported previously (1). After stripping, the aqueous diphosphonic acid has to be thermally degraded for further processing of the actinides, leading to solutions containing high concentrations of phosphoric acid, which, in turn, can generate problems in the successive separation steps for actinides recovery. An alternative procedure is to destroy through wet oxidation the whole resin bed used to sorb the actinides. The wet oxidation of several grams of resin is feasible but is time and reagent consuming. Because of the above mentioned complicated actinide stripping procedures, it may be preferable in some cases to leave the actinides on the resin which becomes a solid waste. In this case it would be preferable that some or all of the polymeric resin matrix be replaced by an inorganic material, to avoid possible generation of gases due to slow radiolytical degradation of the organic polymer. Therefore, a new version of the Diphonix resin has been prepared, where the

chelating diphosphonic acid groups are grafted to a silica support. The new material is called Diphosil, for Diphonix on silica.

Silica grafted aminophosphonic and aminodiphosphonic acids (11) and polyethylene grafted diphosphonic acid (12) materials have been recently reported. The latter paper includes a detailed physico-chemical description of the grafted material, but no metal uptake data are reported.

Objectives of the present work were :

1. to measure the equilibrium and the kinetics of uptake of a number of actinide species and of other metal ions of nuclear, environmental or hydrometallurgical interest by the new Diphosil material.
2. to compare the behavior of the new material with that of the regular Diphonix resin concerning equilibrium and kinetics of metal uptake.
3. to compare the Diphosil and Diphonix resins in their ability to release the extracted metals when in contact with solutions of aqueous soluble diphosphonic acids.

EXPERIMENTAL

Resins

The Diphosil resin was prepared according to the following procedure. In a typical run, 10 g of porous silica (Davisil™, Grade 645, 60-100 mesh size, 300 m²/g surface area, from Aldrich) is dried and subsequently reacted, refluxing for 12 hours, with a mixture of trichloroethylsilane (TCES) and trichlorovinylsilane (TCVS) in 30 mL toluene. After washing with toluene and acetone, the material is dried and grafted with vinylbenzyl chloride (VBC). The grafting procedure is performed by immersing the silica-TCVS/TCES material in a mixture of VBC and azobis(isobutyro)nitrile (AIBN) initiator in toluene, heating at 80 °C for 8 hours under continuous stirring. After this time, the grafted material is washed with toluene and extracted with this solvent for 10 hours. In a separate flask the tetraisopropyl ester of methylenediphosphonic acid is dissolved in toluene and reacted with sodium metal. After the reaction is completed, the VBC grafted silica-TCVS/TCES material is added and the mixture is heated for 24 hours at reflux. The

material is then washed with acetone, acetone/water and water, hydrolysed with 3 M HCl for 3 hours and finally extensively washed with water.

The Diphonix resin in the H⁺ form and 50-100 mesh size was obtained from Eichrom Industries, Inc., Darien, Illinois.

Fig. 1 reports the structure of the two resins, together with an idealized cross section of a single resin bead. Table 1 reports their capacity and density characteristics.

Table 1

Capacity and density of the Diphonix and Diphosil resins

	Diphonix	Diphosil
P capacity (mmol/dry g)	1.64	0.68
H capacity (mmol/dry g)	7.31	1.36
Wet density (g/mL)	1.16	1.50
Bed density (g dry resin/ mL bed)	0.30	0.39

The H⁺ capacities were determined by acid-base titration (13). The much higher H⁺ capacity of the Diphonix resin is due to the presence on the same polymer network of sulfonic and carboxylic acid groups. Because of the hydrophilic nature of the silica support, the introduction of sulfonic groups on the Diphosil material was not required in order to have fast kinetics of metal uptake (*vide infra*). The phosphorus capacity of the Diphonix resin was determined by wet ashing samples of the resins following established procedures (13) and analysing P by ICP-AES (inductively coupled plasma - atomic emission spectrometry). In the case of the Diphosil material, which contains only diphosphonic acid as functional groups, the phosphorus capacity was obtained from the H⁺ capacity. As expected, the P capacity of the Diphosil material is much lower than that of the Diphonix resin, because the diphosphonic acid functional groups of the former resin are only present in a surface layer. In a column configuration, the much lower P capacity of

Diphosil is partly compensated by its higher density, so that one mL bed volume of a Diphosil column has about 50 % of the capacity of one mL bed volume of a Diphonix resin column.

Samples of the resins in H⁺ form were washed extensively with 1 M HNO₃ and water on a Büchner funnel and drained under low vacuum aspiration for about 10 minutes. The resin samples were then stored in tightly closed bottles from which the required amounts were taken for the experiments described. For the determination of their solid content according to the procedure reported in (13), air-dried resin aliquots were weighed, dried overnight at 105 °C and weighed again.

Reagents

Nitric acid solutions were prepared from the Ultrex reagents (J.T.Baker Chemical Co.) and water was obtained from a Milli-Q2 water purification system. All other chemicals were reagent grade and used as received.

²⁴¹Am, ²³⁹Pu, ⁹⁹Tc, ¹⁵²⁻¹⁵⁴Eu, ⁶⁰Co and freshly purified ²³⁰Th and ²³³U were obtained from Argonne stocks. ⁵⁹Fe, ⁶⁵Zn and ⁴⁵Ca were obtained from Isotope Product Laboratories, Burbank, California.

Uptake measurements

The sorption of the above radioisotopes at tracer level concentration from aqueous solutions of different composition by the investigated resins was measured at room temperature (24 ± 1 °C) following the same procedure reported in (1,8). A known volume, typically 1.00 mL, of the aqueous solution containing tracer was equilibrated in a plastic test tube with a weighed amount of the resin (typically 1 - 10 mg). Efficient mixing of the solid and liquid phases was obtained using magnetic microbars (1.5 x 8 mm) rotated at about 200 rpm, which was more than sufficient to prevent the resin particles from settling. A two hours mixing time was used, which is more than that required for equilibrium attainment (*vide infra*). After centrifugation, an aliquot of the solution was withdrawn from the test tube and filtered using a syringe equipped with a PVDF (polyvinylidene difluoride) 0.2 µm pore size membrane filter with a Luer lock (Whatman Laboratory Division, Whatman, Inc., Clifton, New Jersey). Counting of aliquots of the filtered aqueous phase was performed with a Packard Cobra Autogamma counter or via liquid scintillation on a Packard Model 2000 CA counter. Dry weight distribution ratios, D, were calculated as

$$D = \left(\frac{A_o - A_f}{A_f} \right) \left(\frac{V}{w} \right) \quad (1)$$

where A_o and A_f are the aqueous phase activity (cpm) before and after equilibration, respectively, w is the weight of dry resin (g) and V is the volume of the aqueous phase (mL). The weight of the dry resin was calculated by correcting the weighed amount of resin used in the experiments with the experimentally determined solid percent values. When very high values of D were expected, the amount of resin used in the distribution experiments was as small as possible (about 1 mg) in order to have a more easily measurable activity left in the aqueous phase. In the experiments on the uptake of Al(III) an initial metal concentration equal to 1 mM was used and analyses of the metal were performed by ICP-AES. In each experiment the amounts of metal and of resin were chosen in such a way that the resin capacity was always in excess over the metal. In this way resin saturation was never reached. Duplicate experiments showed that the reproducibility of the D measurements was generally within 10 %, although the uncertainty interval was substantially higher for the highest D values ($D \geq 10^3$).

The experiments on uptake kinetics were performed following the same discontinuous technique described previously (4). The primary kinetic data, D vs. time, were normalized by converting them into fractional attainment of equilibrium vs. time data, using eq. 1, following the rationale reported in (4). The kinetic data were then plotted according to the previously derived equation 2 (4) :

$$\ln(1 - F) = -kt \quad (2)$$

where k is the experimentally observed overall rate constant, the fractional attainment of equilibrium, F , is defined as

$$F = \frac{[\bar{M}]_t}{[\bar{M}]_{eq}} \quad (3)$$

and the bar represents the resin phase.

Equation 2 has been reported (14-15) to hold for film-diffusion control with infinite solution volume for the limiting case of isotopic exchange on ion exchange resins. When one of the exchanged species, as in our case, is present at tracer concentration level, all changes in the solution and in the ion-exchanger remain on a trace level and diffusion coefficients, activity coefficients, swelling, composition of

solution and resin, etc. remain practically constant as in the case of isotopic exchange. It has been demonstrated in (14) that the diffusion of the trace ion is always rate-controlling. The rate law derived for film-diffusion control, that is, eq. 2, should thus apply to the kinetic data obtained in this work.

RESULTS AND DISCUSSION

Uptake of metal ions

In comparing the tracer concentration level metal uptake data obtained with the Diphonix and the Diphosil resins, a number of factors must be considered, which can have an effect on the behavior of the two materials with regard to each metal ion.

First of all, the different nature of the two resins is probably going to play an important role. The two resins are shown in idealized form in Figure 1. (Note, however, that the silica used as a starting material for the synthesis of the Diphosil resin is porous. Unlike the idealization of Figure 1, a Diphosil resin bead will likely also contain internal surfaces functionalized with diphosphonic acid groups.) Let us consider, for example, an average bead with a 0.1 mm radius (about 75 mesh size). From simple geometric considerations, and using the density and the phosphorus capacity values of Table 1, it can be calculated that one bead of Diphonix resin contains 0.0040 micromoles of diphosphonic acid groups, compared to 0.0026 micromoles for one bead of Diphosil resin. The diphosphonic acid groups, however, are distributed in a completely different way. In the Diphonix resin they are almost homogeneously dispersed through the whole volume of the bead, while in the Diphosil resin they are concentrated in a surface layer, both internal and external, where the ligand groups will be much more closely packed. Assuming a 10 Ångstrom thickness of the active layer of the Diphosil resin, for example, and using the above reported surface area of the Davisil silica, it can be calculated that the concentration of the diphosphonic acid groups in the surface layer would be at least one order of magnitude larger than the average concentration of ligands in a Diphonix resin bead.

The much larger concentration of ligand groups on the surface of the Diphosil resin will facilitate interaction of incoming metal ions with more than one ligand at the same time, thus favoring complexation of metal ions with a higher charge and more complex coordination geometry, such as the tetravalent actinides. On the other hand, the benzene ring separated by a CH_2 group from the

diphosphonic acid group of the Diphosil material will somewhat reduce the basicity of the P=O group, reducing the tendency of the ligand for metal complexation.

Finally, the presence of other functional groups on the Diphonix resin, such as the sulfonic acid group, may play a role in the binding of metals. The sulfonic acid groups may take part in metal uptake by providing negatively charged sites which can contribute to the metal charge neutralization. (A similar role by the carboxylic acid groups also present on the Diphonix resin can be excluded in the present study because the aqueous acidity used in the experiment was always at least 0.01 M). Regarding the Diphosil resin, moreover, a possible contribution of the support silica surface to the interaction with metal species cannot be excluded but is unlikely at the acidities studied.

All these factors, that is, basicity, concentration and packing of the ligand, coordination number and geometry of the metal species, charge neutralization requirements, surface reaction (Diphosil) vs. involvement of bulk material (Diphonix), make a complete description of the interaction between the two resins and metal ions quite difficult and the relative behavior of each single metal species almost unpredictable.

This is clearly illustrated in Figures 2, 3 and 4. Figure 2 shows a comparison of the uptake of actinide species by the two resins measured as function of the aqueous acidity. While for Am(III) and U(VI) the data show little change in going from the Diphonix to the Diphosil resin, with the former exhibiting slightly higher values, the previously anticipated higher uptake of tetravalent actinides is clearly shown by the Pu(IV) data. The Th(IV) data show that the uptake by the Diphosil material is much less sensitive to the acidity than with the Diphonix resin. The slow decline of the D values of tetravalent actinides in the range of high aqueous nitric acid concentrations has been explained in (1) as mostly due to the competition of nitric acid with the metal for the phosphoryl groups of the resin. This competition should be less effective if the basicity of the phosphoryl groups is reduced, in agreement with the trend indicated by the Th(IV)-Diphosil data.

Figure 3 reports similar data for Eu(III), Tc(VII), Al(III) and Fe(III). Not surprisingly, the behavior of Eu(III) with the two resins is very much the same as that of Am(III), therefore, whatever is the combination of factors that brings about almost the same uptake values of the two resins with Am(III), the same combination of factors holds for Eu(III) as well.

The Tc(VII) data have been included in this study not because of their practical usefulness (with either resin the D values are too small for any possible

application), but because they can provide further information on the chemistry of metal uptake by the resins. The data show two interesting features, i.e., first, with both resins the D values increase in the highest acidity range with a pronounced minimum at about 2-3 M HNO₃, and, second, the Diphosil resin data are consistently lower than the Diphonix resin data in the whole range of HNO₃ concentrations. Tc(VII) exists in solution as the pertechnetate anion TcO₄⁻, whose parent pertechnetetic acid is a quite strong acid (16). The minimum in the acid dependencies of both resins is with all probability due to the hydrogen bonding of undissociated HTcO₄ to the phosphoryl groups of the diphosphonic acid. As previously discussed (8), the increased uptake of TcO₄⁻ by the two resins at high HNO₃ concentrations is an experimental evidence of the interaction of strong acids with the phosphoryl groups of the diphosphonic acid, and lends support to the hypothesis that the decline of the distribution ratios of tetravalent actinides above 3 M nitric acid is due to the competition of the aqueous acid with the metal species for the available P=O groups. The second feature of the Tc(VII) data, that is, the lower D values for the Diphosil resin, is probably again a consequence of the lower basicity of the Diphosil resin P=O groups.

Most interesting is the comparison of the uptake data of Al(III) and Fe(III) shown in the lower half of Fig. 3. The Diphosil resin exhibits a much higher affinity for trivalent iron and a much lower affinity for aluminum relative to the Diphonix resin. It is known that aqueous soluble diphosphonic acids form stronger complexes with iron (III) than with aluminum. For example, with methylenediphosphonic acid (MDPA), 1:1 and 1:2 complexes are reported with log β values equal to 19.9 and 26.6 for Fe(III) and to 14.1 and 23.0 for Al(III) (17). Thus, a better complexation of Fe(III) over Al(III) by the two resins is expected and indeed verified. However, the Diphosil resin seems to magnify the difference in complexation of the two metal species by the diphosphonic acid group. This, in turn, may be an indication that in the Diphonix resin the sulfonic acid groups also play a role in the binding of Al(III), role which would obviously be absent in the case of the Diphosil resin. As already discussed in the case of Th(IV), the Fe(III)-Diphosil D values in the high acidity range do not drop with increasing acidity. Again, this can be explained by the reduced competition of the acid with the metal for the less basic P=O groups of the Diphosil resin.

Figure 4 reports the data obtained in the uptake of some divalent cations by the two resins. All three investigated cations, Ca(II), Zn(II) and Co(II), exhibit the same behavior, that is, substantially lower D values with the Diphosil resin. It is again difficult to attribute this behavior to a single predominating reason. The most obvious explanation would be the involvement of the sulfonic groups of the Diphonix resin in the uptake of these metals. Yet, at least in the case of the alkali

earth cations, it has been demonstrated previously (7), based on the identical relative affinity measured with the two resins for the cations of the series Ca, Sr, Ba, and Ra, that in the Diphonix resin the cations are bound mainly to the diphosphonic acid groups.

Effect of matrix constituents

To fully exploit the properties of the Diphosil resin for actinide separations, one must take into account how other commonly occurring constituents, both cationic and anionic, influence the uptake of actinide ions of interest. A similar investigation has been reported previously for the Diphonix resin (5,6).

Figure 5 reports the data obtained in the uptake of Am(III), U(VI), Pu(IV) and Th(IV) by the Diphosil resin in the presence of large concentrations of NaNO₃ at two aqueous acidities. The data show that a significant reduction of the D values is observed only for Am(III) in the NaNO₃ concentration range above 1 M. The measured Am(III) distribution ratios, however, are still high enough for practical applications even when the solution is 4 M in NaNO₃. The results of Figure 5 are fully consistent with those reported previously for the Diphonix resin (5).

The effect of high concentrations of Ca(II) on the uptake of actinides by the Diphosil resin has not been measured, because we have shown previously (5) that Ca(II) has very little effect on the uptake of the actinides by the Diphonix resin. Also, we have reported in Figure 4, discussed earlier, that the Diphosil resin has a lower affinity for Ca(II) than Diphonix resin, which means that an even smaller interference by Ca(II) on the uptake of actinides with the former resin is expected. As for the Diphonix resin, the ability of the Diphosil resin to strongly sorb actinides from high concentrations of sodium and calcium salts solutions containing a wide range of acidities suggests a number of applications in waste processing and ground and surface water decontamination.

Much more important are the data of Figure 6 showing the effect of increasing concentrations of Al(III) and Fe(III) on the uptake of actinides by the Diphonix and the Diphosil resin. Both cations are strongly retained by the resins and therefore a profound effect on the retention of actinides is expected. Regarding Al(III), it was shown in (5) that the uptake of Th(IV) and U(VI) by the Diphonix resin was somewhat reduced, but the distribution ratios of the metal cations were still above 10³ for an Al(III) concentrations of 0.1 M. A similar or better behavior is expected for the Diphosil resin, which, as discussed earlier, exhibits a lower affinity for Al(III). Much stronger is the effect of Al(III) on the uptake of Am(III), as shown

in the upper half of Figure 6. This effect seems to be slightly worse for the Diphosil resin, which on one hand is less sensitive to the presence of Al(III), but on the other hand also has a reduced affinity for Am(III) (see Figure 2). While with the Diphonix resin the presence of aluminum can be counteracted by adding fluoride ions (5), obviously with the Diphosil resin this is not possible. Consequently, the real limit to the use of Diphosil for Am(III) uptake is the concentration of aluminum in the solution of interest. This concentration should be lower than about 0.01 M.

The effect of Fe(III) on the uptake of the actinide ions is reported in the lower half of Figure 6. As expected, concentrations of iron (III) above 0.01 M make the resins totally ineffective for Am(III) uptake and have quite a detrimental effect also on the uptake of U(VI) and even of Th(IV). The effect is substantially more pronounced with the Diphosil resin, which shows a higher uptake of Fe(III) (see Figure 3). Fortunately, however, the presence of Fe(III) in the system can be avoided by reducing the interfering ion to the much less extractable Fe(II). In the presence of ascorbic acid, in fact, Am(III) can be quite efficiently sorbed by either resin even at iron concentrations approaching 0.1 M.

Figure 7 reports the effect of oxalic acid on the uptake of Am(III), U(VI), Th(IV) and Fe(III) by the Diphosil resin at two different acidities. Particularly remarkable is the fact that a 1 M solution of oxalic acid has practically no effect on the uptake of Th(IV) and little effect on the uptake of U(VI) and Am(III). Similar results obtained with the Diphonix resin have been discussed in detail previously (6) and have been semi-quantitatively explained by assuming the simultaneous sorption of uncomplexed cations and of neutral metal oxalato-complexes. We believe that the Diphosil resin behaves essentially in the same way. Although the effect of other complexing anions, such as sulfate and phosphate ions, on the uptake of actinide ions by the Diphosil resin has not been measured, it is very likely that the results reported for the Diphonix resin in (6) can be extended to the Diphosil resin as well.

Kinetics of metal uptake

Figures 8 and 9 report the rate of uptake of Am(III), U(IV), Th(IV) and Fe(III) by the Diphonix and the Diphosil resins. The data are plotted according to eq. 2, that is, in the form of fractional attainment of equilibrium vs time plots. The data show that in most cases about 99% of the equilibrium distribution is reached within 5 - 10 minutes of contact, that is, with both resins, and especially with the Diphosil one, the uptake of metal species at tracer concentration level is very rapid. From a more general point of view, the data show, as expected based on the very low metal concentration, that the metal uptake is film-diffusion controlled for at

least 90 % of the process. The porous nature of the silica support and the previously mentioned probable presence in the beads of Diphosil of some internal functionalized surfaces are probably responsible for the deviations of the data from linearity in the final fraction of equilibrium attainment.

An interesting feature of the data of Figures 8 and 9 is that the metal uptake is always faster at the lower concentrations of aqueous acid, that is when the equilibrium distribution ratio is higher. This phenomenon, particularly evident with Am(III), whose acid dependency curves with either resin are steeper, can be interpreted as the effect of selectivity on the ion exchange rate. A complete discussion of this effect, which is typically met when the ion exchange process is film-diffusion controlled, can be found in (15). Similar results obtained with the Diphonix resin have been previously reported and discussed in detail (4). Here it is worth mentioning that the effect is larger with the Diphonix than with the Diphosil resin. The reason for this difference can be understood considering the different nature of the two resins as schematized ideally in Figure 1. With the Diphosil resin, the metal ions react essentially only with the ligands contained in a surface layer, and the resin bead is not penetrated by the external solution. The different kinetic behavior at the different acidities is then the true selectivity effect on the rate of uptake. With the Diphonix resin, on the other hand, the metal uptake is accompanied by the resin swelling, which is larger for more diluted external solutions. Thus, at 0.1 M HNO₃, the metal uptake is accelerated by the external aqueous solutions being transferred inside the bead under the osmotic pressure gradient. Consequently, the kinetic data obtained with the Diphonix resin and diluted external solutions are the result of the overlapping of two different phenomena, that is, resin swelling and film-diffusion.

Stripping of actinide ions

It was anticipated in (1) that the only effective stripping agents of actinide ions from the Diphonix resin are compounds belonging to the family of aqueous soluble diphosphonic acids, which contain the same ligand group as the resin. Some uptake data from solutions of the 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) were reported in (1). A more complete investigation is reported in the present work.

Figure 10 reports the uptake of Am(III), U(VI), Pu(IV) and Th(IV) from HEDPA solutions by the Diphonix and the Diphosil resin. Although these data have not been obtained in actual column stripping experiments, it is justified to assume that the lower the distribution ratios of Figure 10, the easier should be to strip the actinides with the corresponding HEDPA solutions. The Diphonix resin data (left

half of Figure 10) show that HEDPA is actually very effective in stripping the actinides, especially the tetravalent ones, a 0.1 M HEDPA solution being sufficient to have D values of Th(IV) and Pu(IV) below 0.1. This is not surprising considering the extraordinarily strong complexes formed in aqueous solution between HEDPA and Th(IV) (16). Am(III) is the most difficult actinide to strip from the Diphonix resin, requiring at least a 0.5 M HEDPA solution, because it the least strongly complexed by HEDPA. The situation is somewhat different with the Diphosil resin, reflecting the actinide uptake data reported in Figure 2. While the behavior of Am(III) and U(VI) does not change significantly in shifting from the Diphonix to the Diphosil resin, the tetravalent actinide species become the most difficult to strip with the latter resin. In other words, because the Diphosil resin exhibits a higher affinity for the tetravalent actinides, a higher concentration of aqueous HEDPA is required to remove those elements from the resin. As a result, the overall stripping of the actinides from the Diphosil resin, although not impossible, appears to be more difficult than with the Diphonix resin. It should be kept in mind that a higher concentration of HEDPA in the strip solution means that, for further processing of the actinides, more time and reagent consuming degradation procedures of the aqueous diphosphonic acid will be needed. The higher concentration of HEDPA would in turn generate larger volumes of waste solutions. From these considerations it appears that the use of the Diphosil resin for the isolation of actinides should essentially be considered only when the subsequent recovery of the actinides is not required.

CONCLUSIONS

The Diphosil resin is a new material containing geminally substituted diphosphonic acid chelating groups grafted to a silica support. The equilibrium and kinetics of the uptake of actinide ions by the new resin have been measured in a variety of conditions and compared with those of the previously investigated Diphonix resin, where the same ligand groups are bonded to a styrene-based polymeric matrix.

The measurements reported in this paper have allowed us to conclude that :

1. The Diphosil resin exhibits an even higher affinity for tetravalent actinides than the Diphonix resin. The uptake of tri- and hexa-valent actinides is essentially the same for the two resins.
2. The divalent cations investigated, that is Ca(II), Zn(II) and Co(II), are all substantially less sorbed by the Diphosil resin. Among the trivalent cations,

Al(III) is less sorbed and Fe(III) is more sorbed by the Diphosil as compared to the Diphonix resin.

3. The Diphosil resin sorbs the actinide ions at trace concentration level very rapidly even at high acidities, in spite of the lack of swelling.
4. Large concentrations of sodium and calcium ions have practically no effect on the uptake of actinides by the Diphosil resin. In the uptake of Am(III), the presence of aluminum can be tolerated only up to a maximum concentration of 0.01 M. Fe(III), if present, should always be reduced to Fe(II) to minimize the competition of iron with the actinides. Large concentrations of oxalic, sulfuric and phosphoric acid have little effect on the uptake of actinides.
5. The stripping of actinides from the Diphosil resin is even more difficult than from the Diphonix resin, and can be accomplished only using aqueous soluble diphosphonic acids at concentrations above 1 M.
6. Based on the above results, the Diphosil resin appears particularly well suited for those cases where the recovery and further processing of the sorbed actinides is not required and the loaded resin can be considered as a solid waste. Because about 90 % of the Diphosil weight is silica, the problem of possible generation of gaseous compounds due to the slow radiolytical degradation of the organic components of the resin is minimized.

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REFERENCES

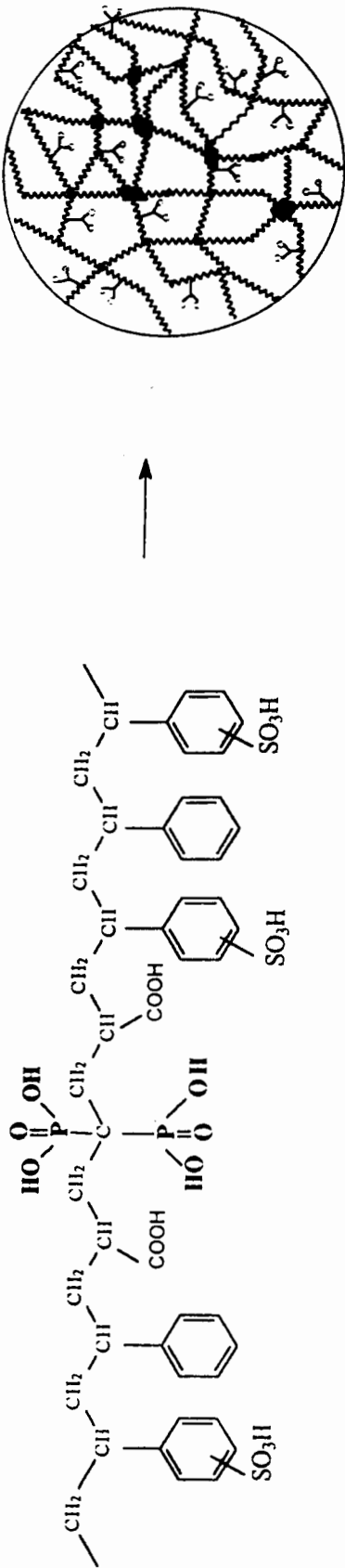
1. E. P. Horwitz, R. Chiarizia, H. Diamond, R. C. Gatrone, S. D. Alexandratos, A. W. Trochimzuk and D. W. Creek, *Solvent Extr. Ion Exch.*, 11(5), 943 (1993).
2. R. Chiarizia, E. P. Horwitz, R. C. Gatrone, S. D. Alexandratos, A. W. Trochimzuk and D. W. Creek, *Solvent Extr. Ion Exch.*, 11(5), 967 (1993).
3. K. L. Nash, P. G. Rickert, J. V. Muntean and S. D. Alexandratos, *Solvent Extr. Ion Exch.*, 12(1), 193 (1994).
4. R. Chiarizia, E. P. Horwitz and S. D. Alexandratos, *Solvent Extr. Ion Exch.*, 12(1), 211 (1994).
5. E. P. Horwitz, R. Chiarizia and S. D. Alexandratos, *Solvent Extr. Ion Exch.*, 12(4), 831 (1994).
6. R. Chiarizia and E. P. Horwitz, *Solvent Extr. Ion Exch.*, 12(4), 847 (1994).
7. R. Chiarizia, J. R. Ferraro, K. A. D'Arcy and E. P. Horwitz, *Solvent Extr. Ion Exch.*, 13(6), 1063 (1995).
8. R. Chiarizia, K. A. D'Arcy, E. P. Horwitz, S. D. Alexandratos and A. W. Trochimczuk, *Uptake of Metal Ions by a New Chelating Ion Exchange Resin. Part 8 : Simultaneous Uptake of Cationic and Anionic Species*, *Solvent Extr. Ion Exch.*, 14(3) (1995), in press.
9. J. J. Hines, H. Diamond, J. E. Young, W. Mulac, R. Chiarizia and E. P. Horwitz, *Separ. Sci. Technol.*, 30 (7-9), 1373 (1995).
10. L. Smith, J. S. Crain, J. S. Yaeger, E. P. Horwitz, H. Diamond and R. Chiarizia, *J. Radioanal. Nucl. Chem.*, 194(1), 151 (1995).
11. Yu. V. Kholin, V. N. Zaitsev, G. N. Zaitseva, L. S. Vasilik and S. A. Mernyi, *Russian J. Inorg. Chem.*, 40(2), 261 (1995).
12. M. J. Sundell, K. B. Ekman, B. L. Svarfvar and J. H. Nasman, *Reactive Polymers*, 25, 1 (1995).

13. J. Korkish, Handbook of Ion Exchange Resins : Their Application to Inorganic Analytical Chemistry, CRC Press, Boca Raton, Florida, 1989.
14. F. Helfferich, Ion Exchange Kinetics in Ion-Exchange, J. A. Marinsky, Ed., vol.1, chap.2, Marcel Dekker, New York, 1966.
15. F. Helfferich, Ion Exchange, Mc Graw - Hill, New York, 1962.
16. K. R. Ashley, J. R. Ball, A. B. Pinkerton, K. D. Abney and N. C. Schroeder, Solvent Extr. Ion Exch., 12(2), 239 (1994).
17. E .N. Rizkalla, Reviews in Inorg. Chem., 5(3), 223 (1983).

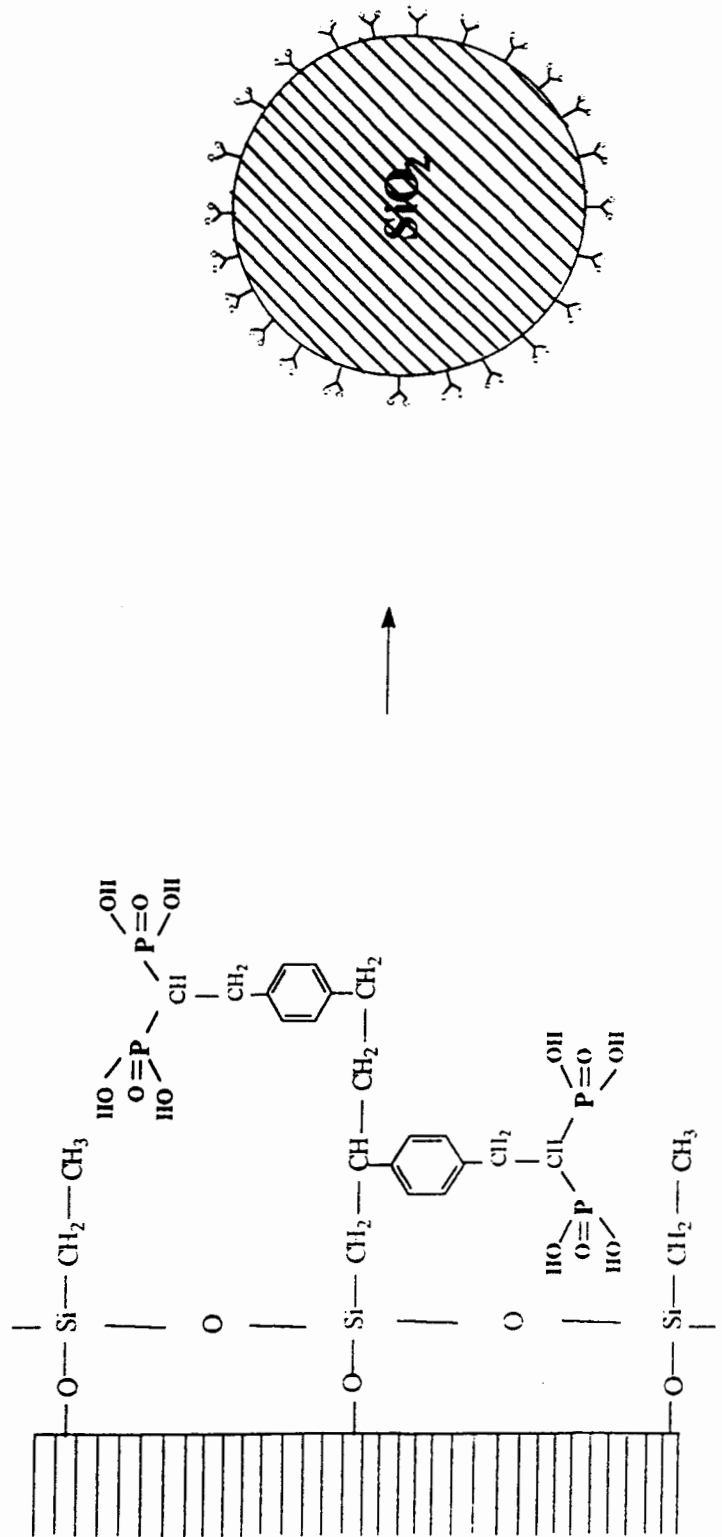
Figure Captions

- Figure 1 : Chemical structures and idealized cross sections of a single bead of the Diphonix and Diphosil resins.
- Figure 2 : Comparison of the uptake of Am(III), U(VI), Pu(IV) and Th(IV) by the Diphonix and the Diphosil resins from nitric acid solutions.
- Figure 3 : Comparison of the uptake of Eu(III), TcO_4^- , Al(III) and Fe(III) by the Diphonix and the Diphosil resins from nitric acid solutions.
- Figure 4 : Comparison of the uptake of Ca(II), Zn(II) and Co(II) by the Diphonix and the Diphosil resins from nitric acid solutions.
- Figure 5 : Effect of NaNO_3 on the uptake of Am(III), U(VI), Pu(IV) and Th(IV) by the Diphosil resins from 0.1 and 1 M HNO_3 .
- Figure 6 : Upper half : effect of Al(III) on the uptake of Am(III) by the Diphonix and the Diphosil resins from various concentrations of HCl or HNO_3 ; Lower half : effect of Fe(III) on the uptake of Am(III), U(VI), and Th(IV) by the Diphonix and the Diphosil resins from 1 M HNO_3 . Also reported are data obtained with the system Am(III)-Fe(III)-Ascorbic Acid.
- Figure 7 : Effect of oxalic acid on the uptake of Am(III), U(VI), Th(IV) and Fe(III) by the Diphosil resin from 0.1 and 1 M HNO_3 .
- Figure 8 : Kinetics of Am(III) (upper half) and of U(VI) (lower half) uptake by the Diphonix and the Diphosil resins at 0.1, 1 and 5 M HNO_3 .
- Figure 9 : Kinetics of Th(IV) (upper half) and of Fe(III) (lower half) uptake by the Diphonix and the Diphosil resins at 0.1, 1 and 5 or 6 M HNO_3 .
- Figure 10: Comparison of the uptake of Am(III), U(VI), Pu(IV) and Th(IV) by the Diphonix and the Diphosil resins from 1-hydroxyethane-1,1-diphosphonic acid solutions.

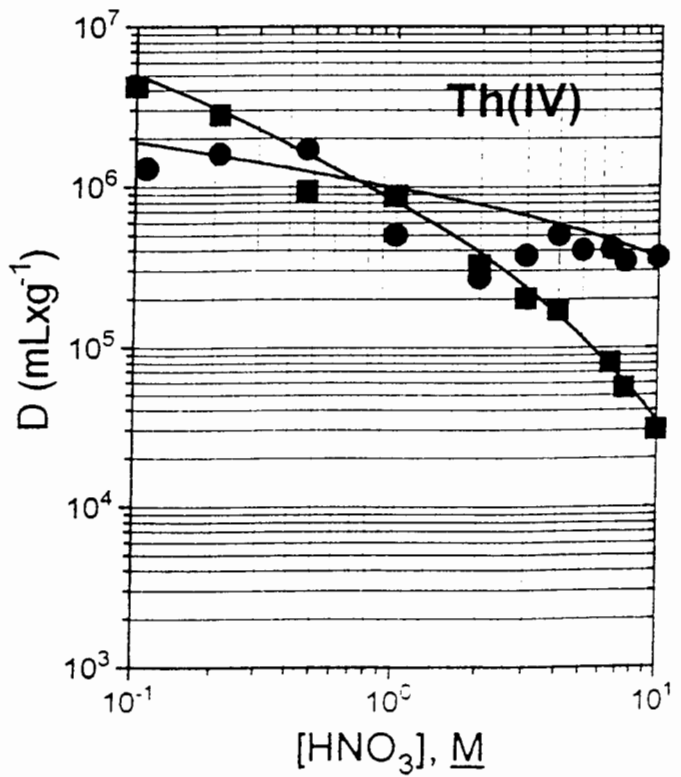
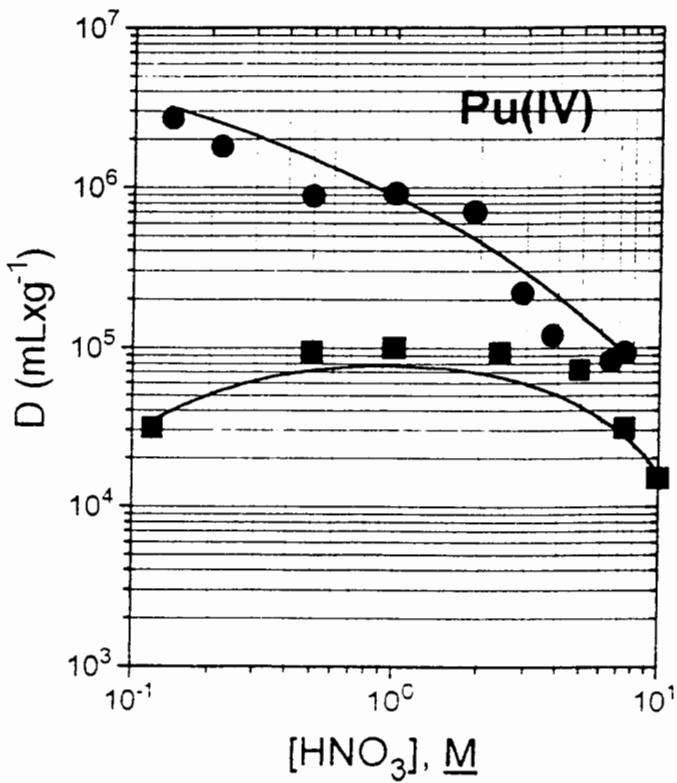
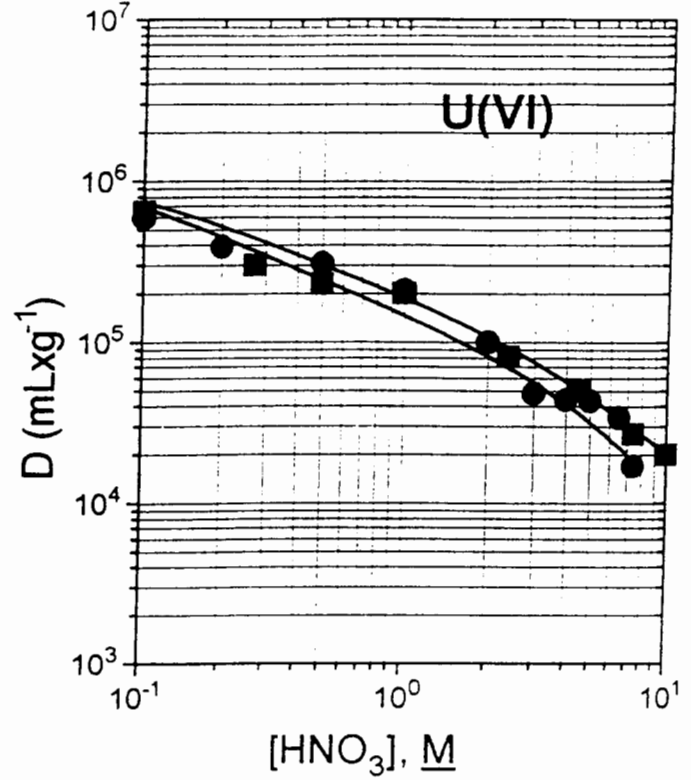
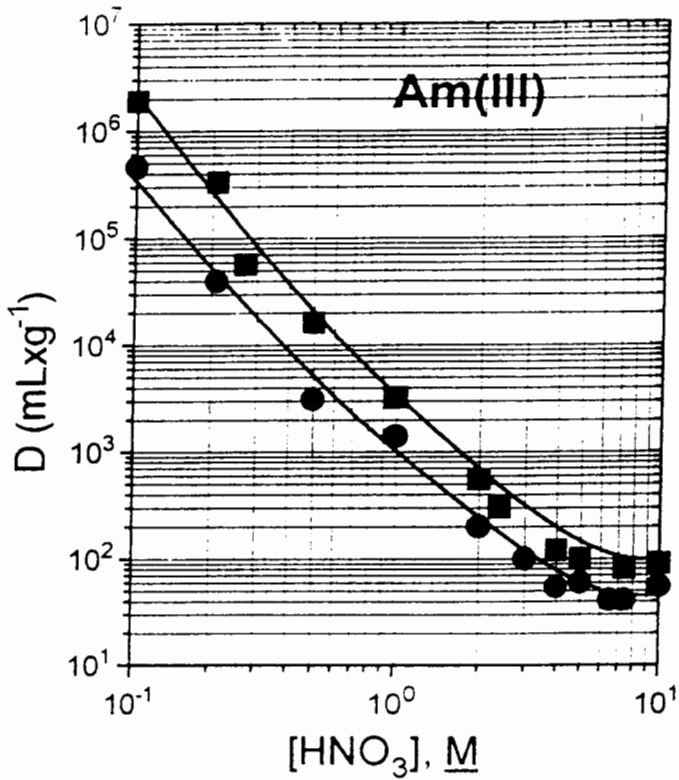
DIPHONIX RESIN



DIPHOSIL RESIN



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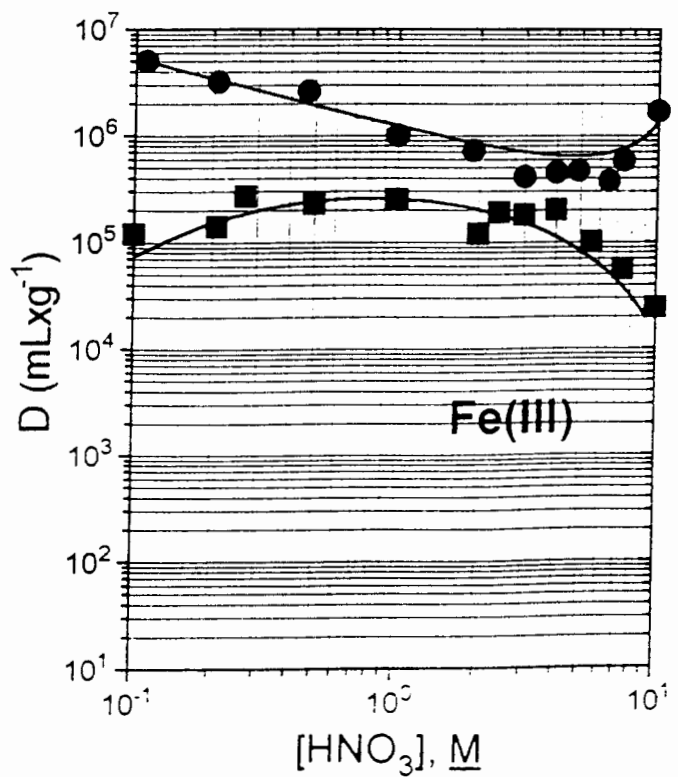
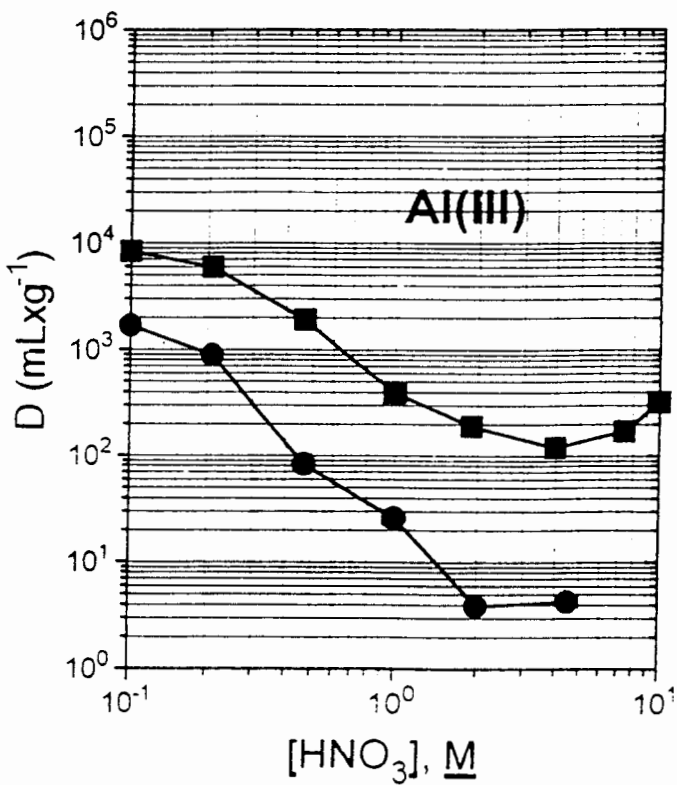
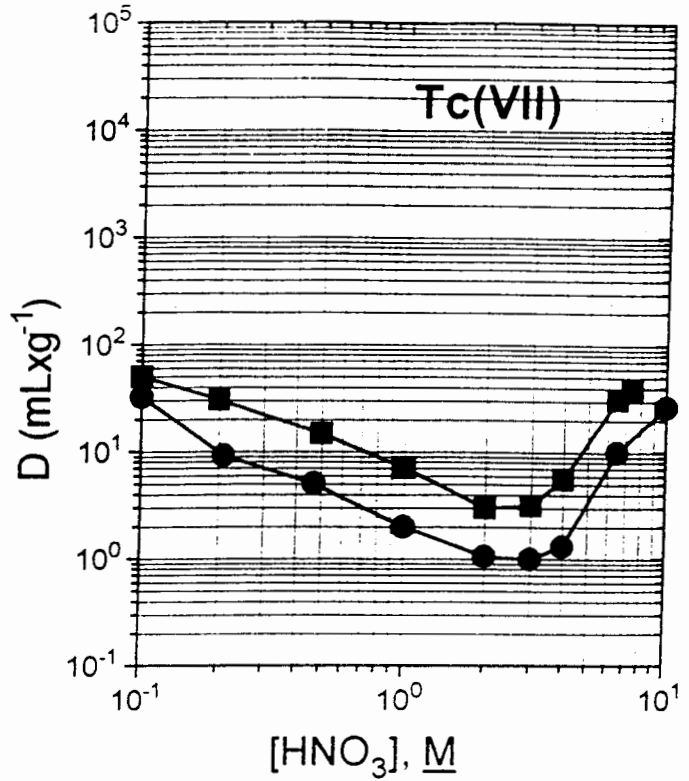
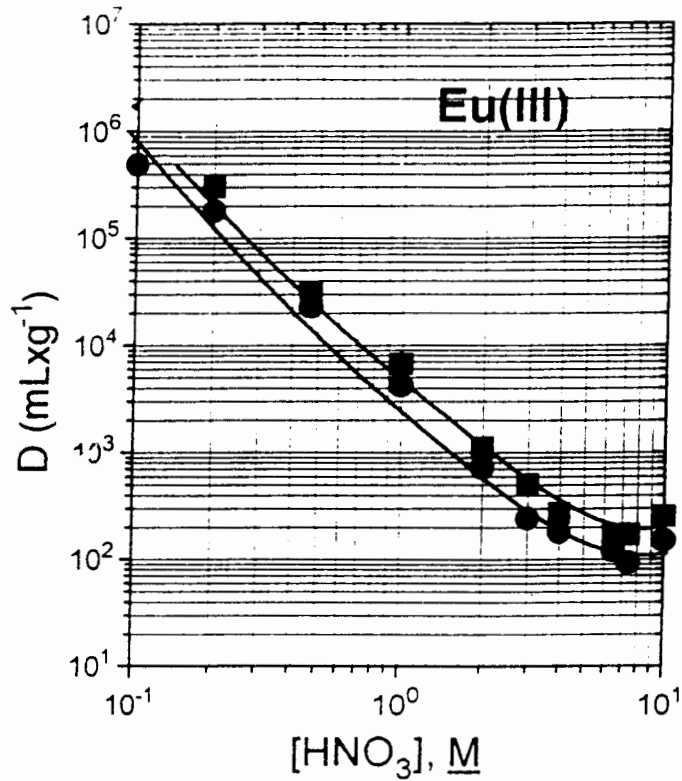


Fig. 3

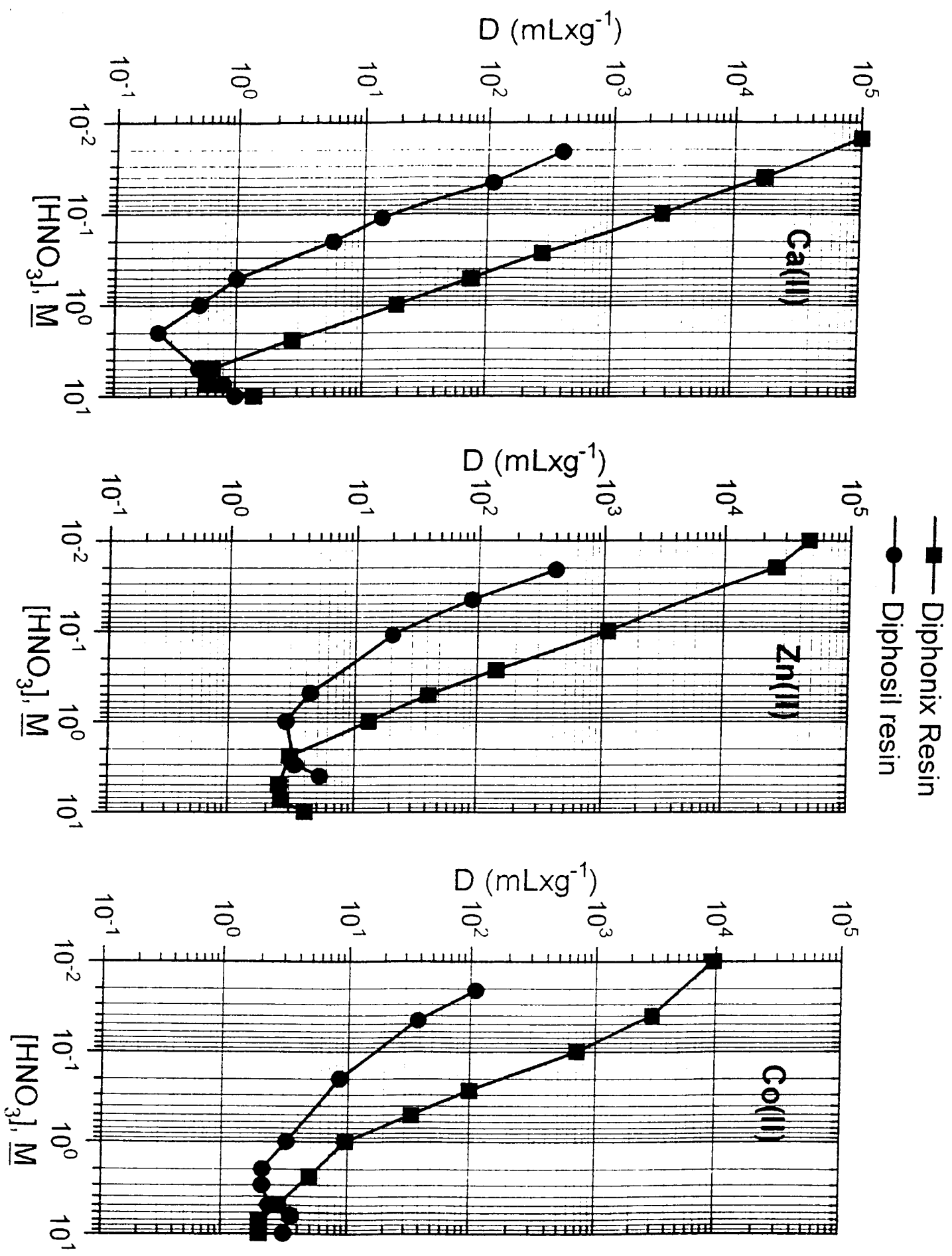
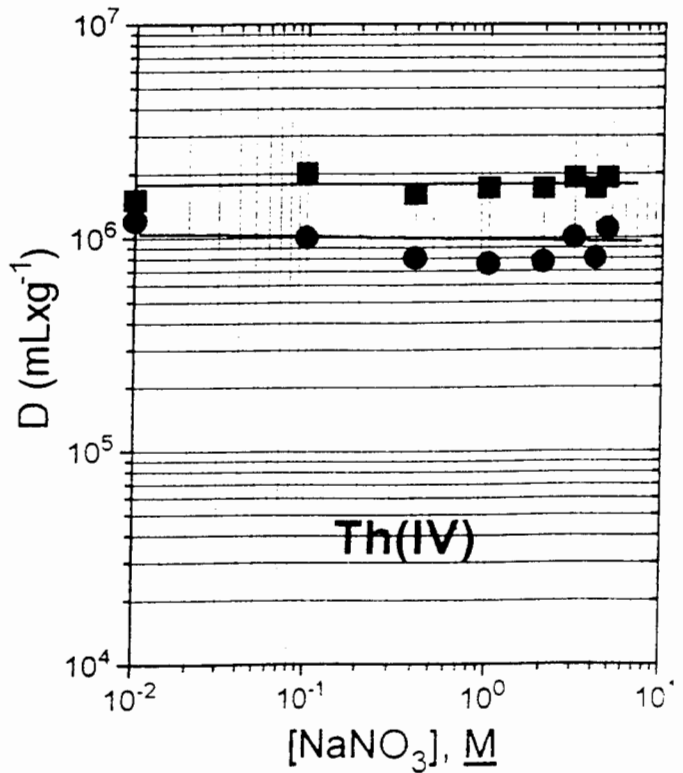
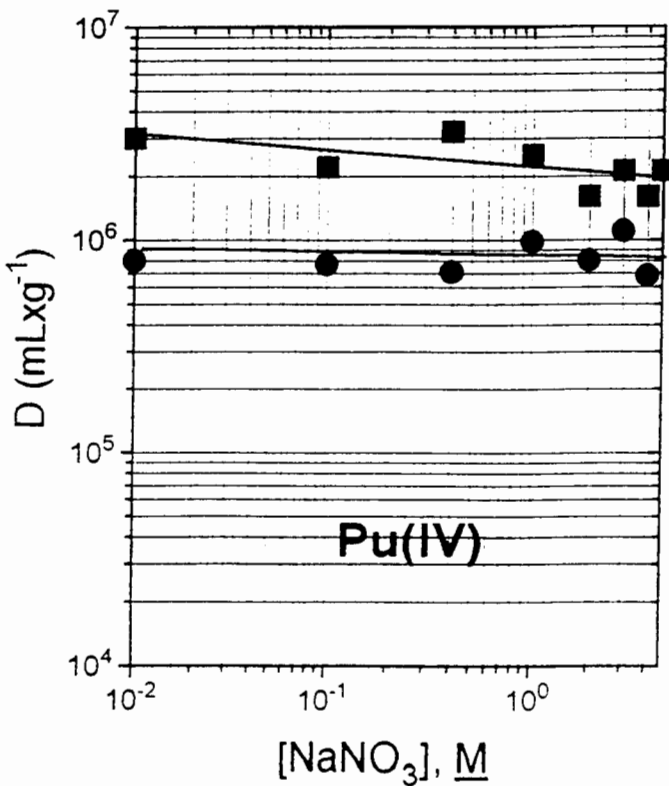
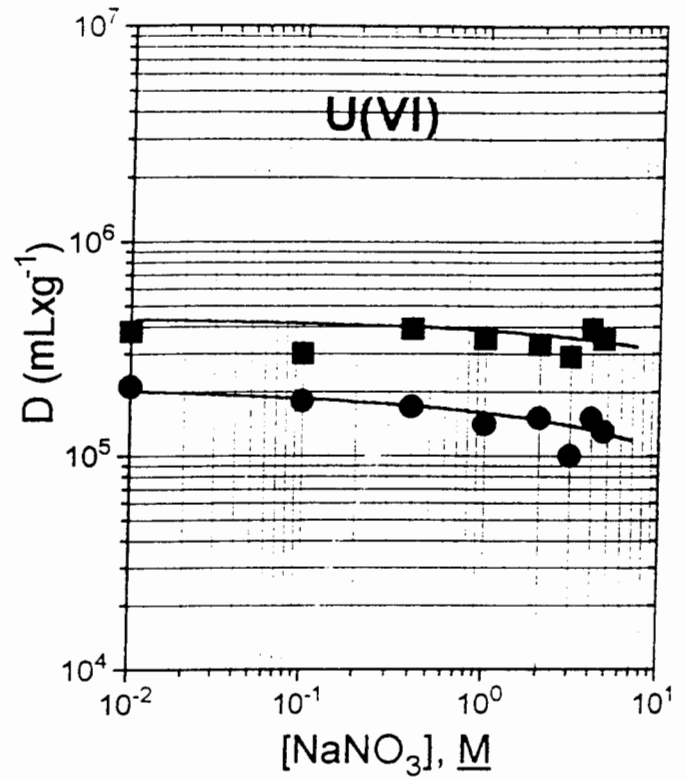
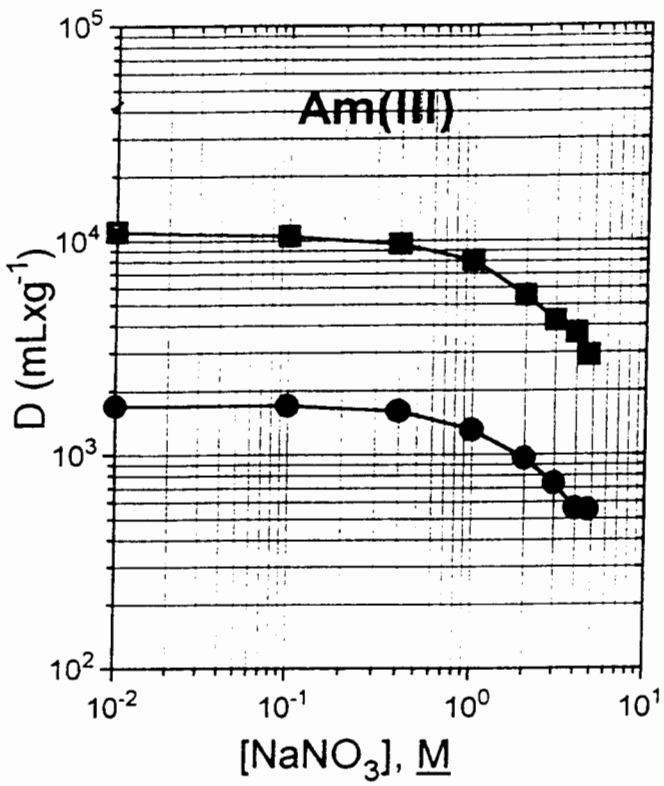


Fig -

—■— 0.1 M HNO₃
—●— 1 M HNO₃



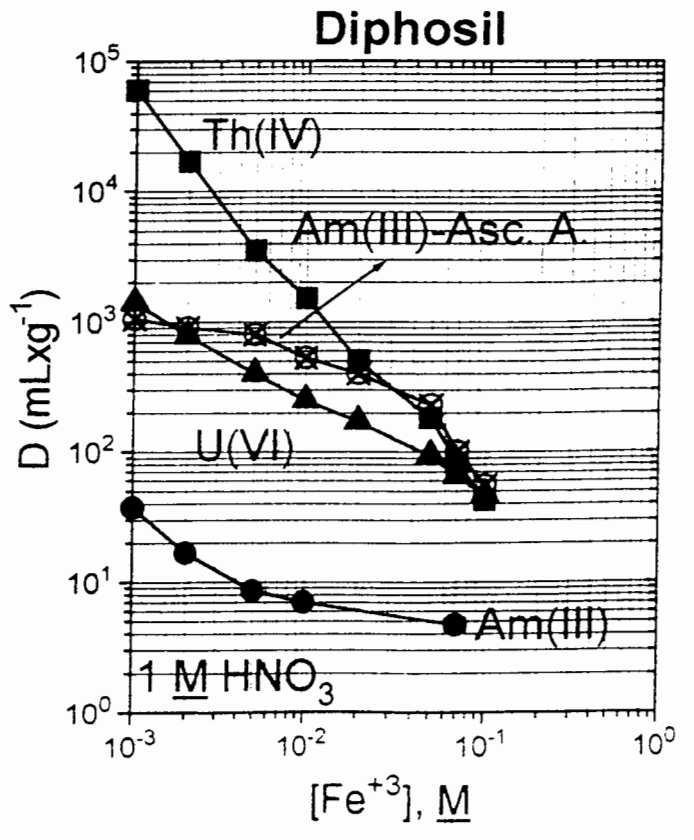
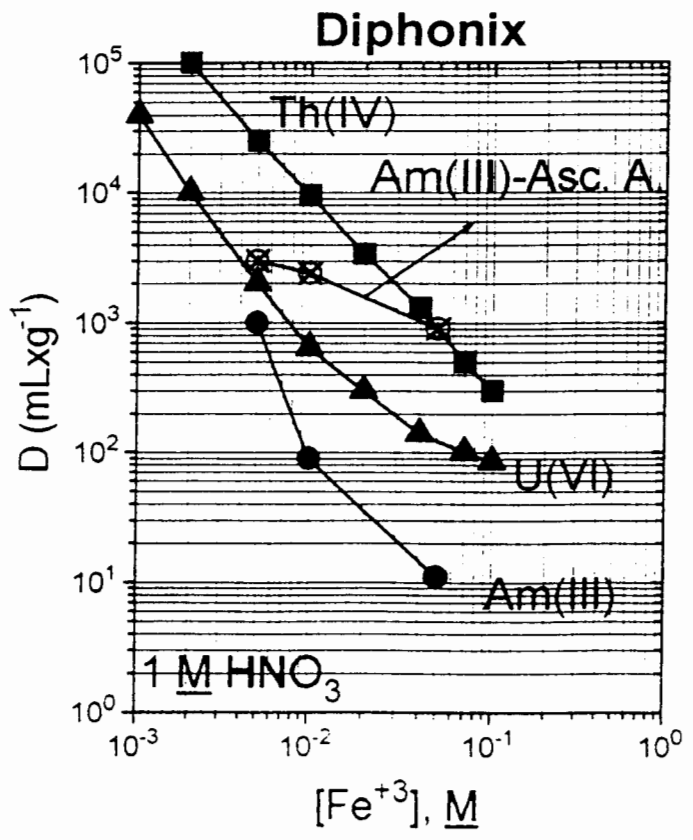
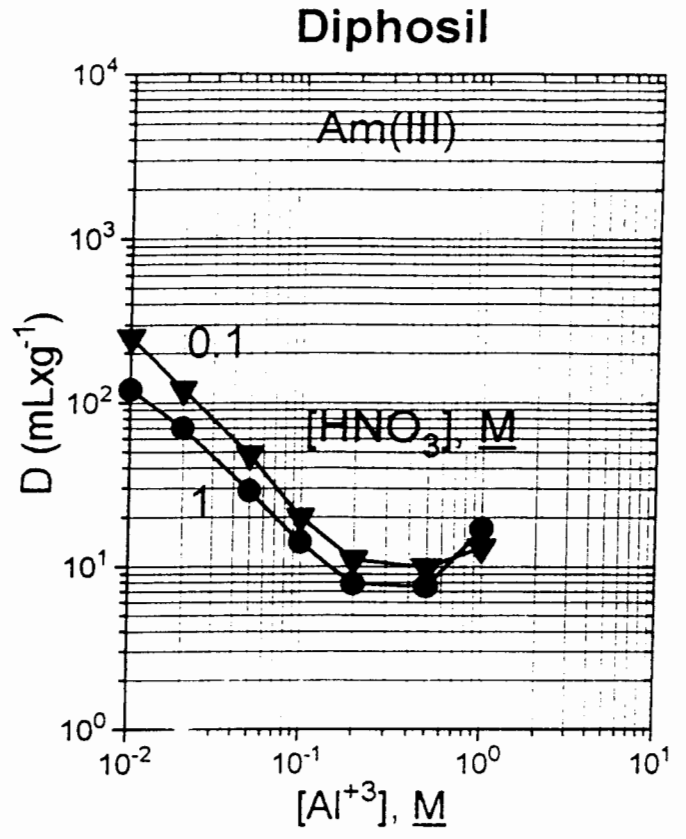
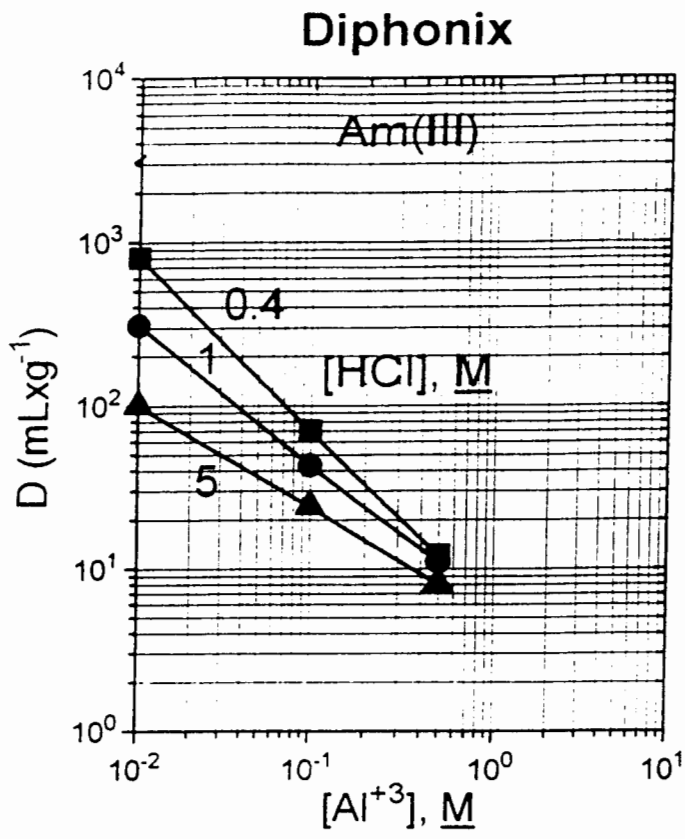


Fig. 6

—■— 0.1 M HNO₃
 —●— 1 M HNO₃

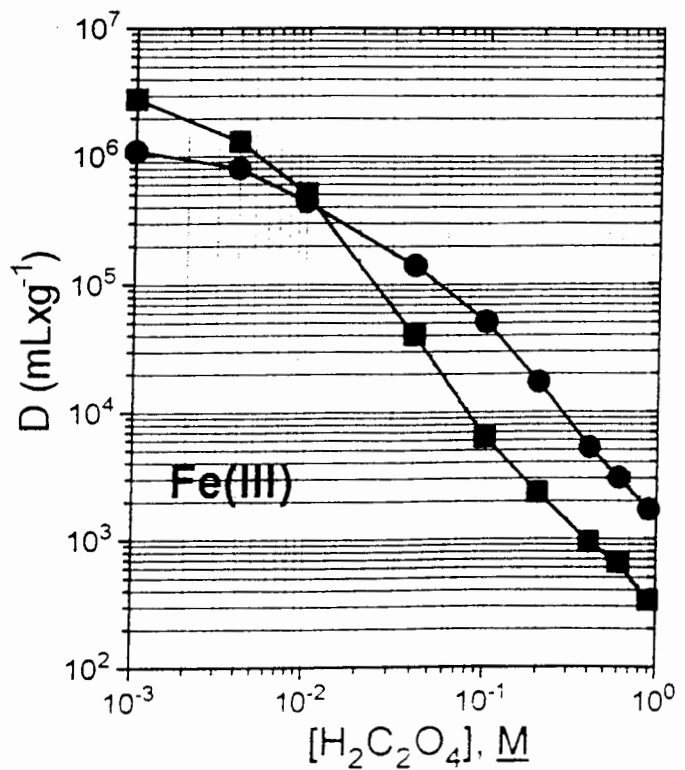
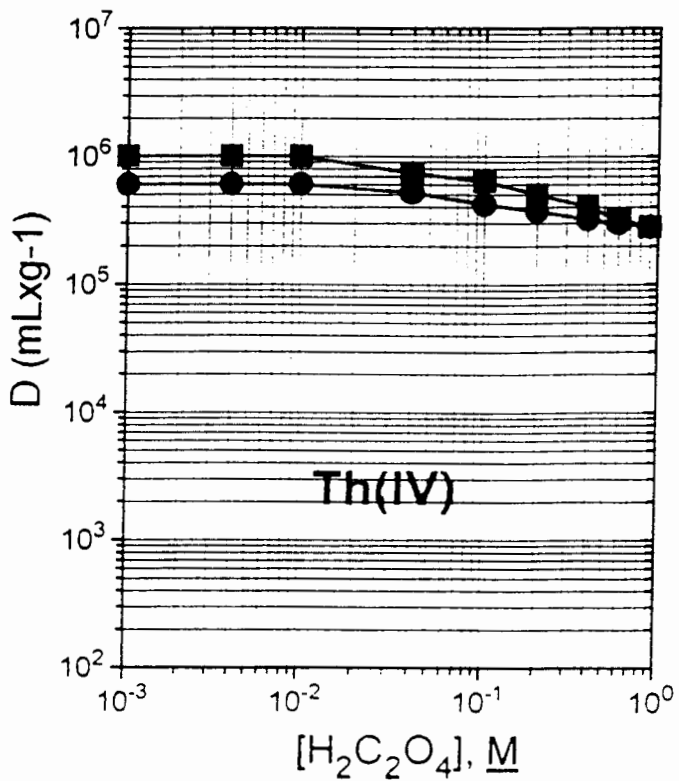
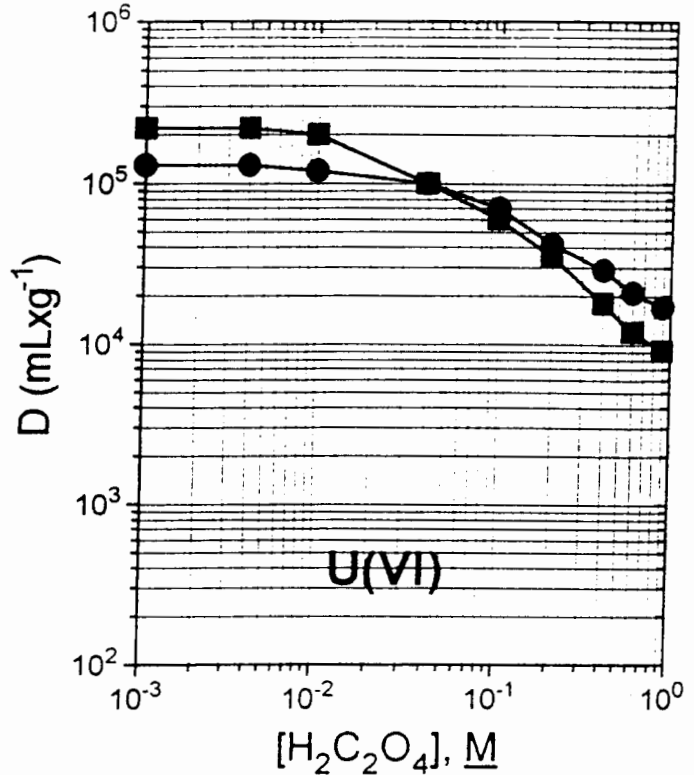
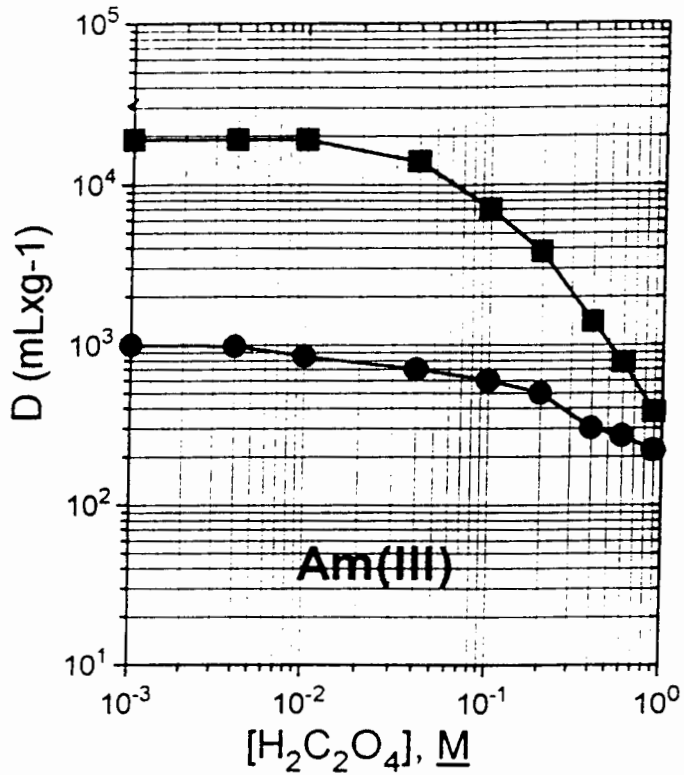
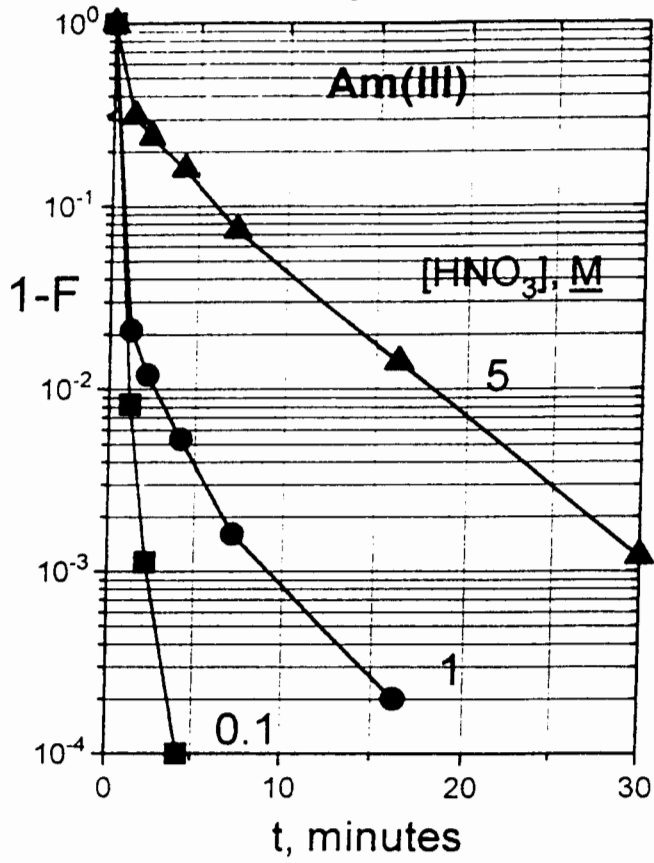
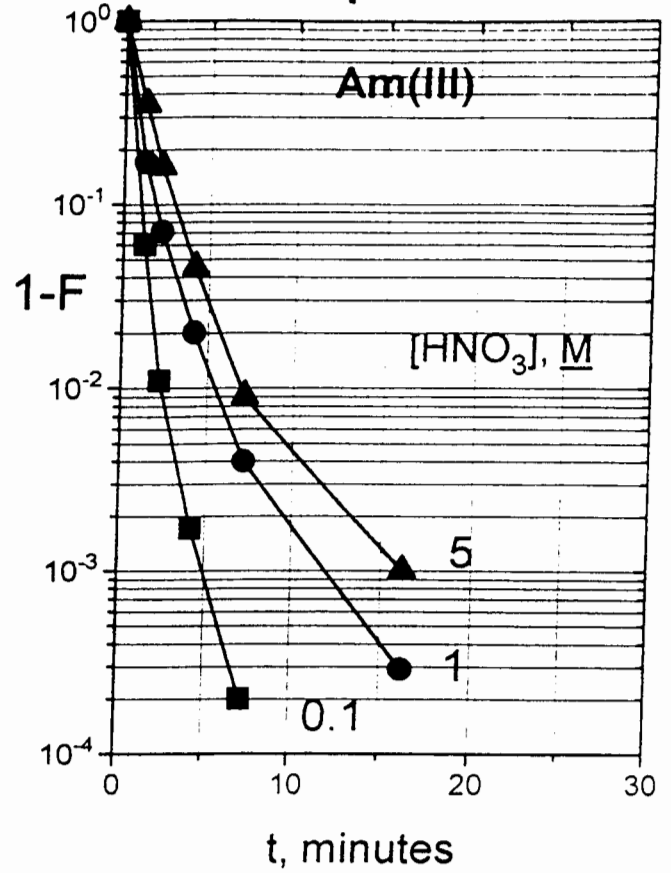


Fig. 7

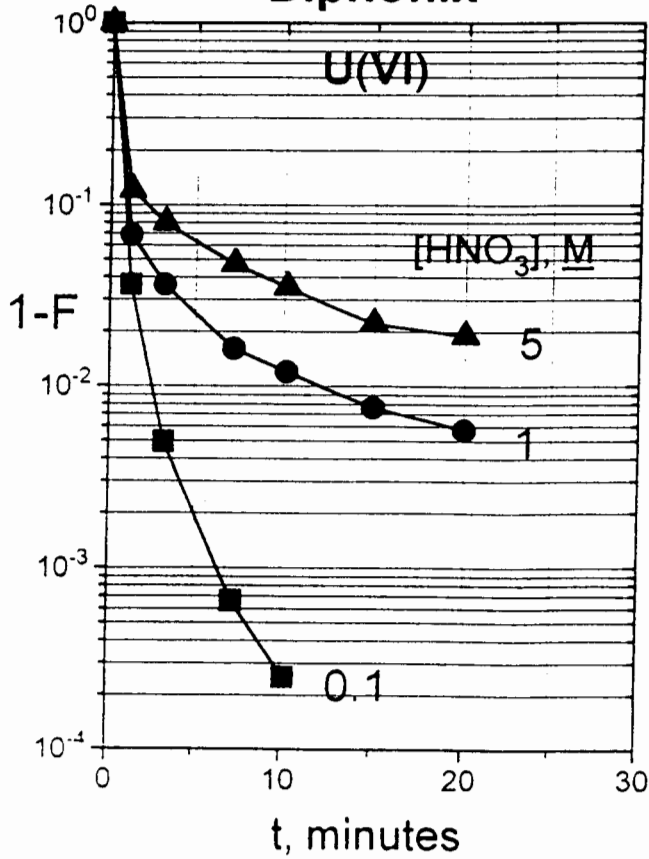
Diphonix



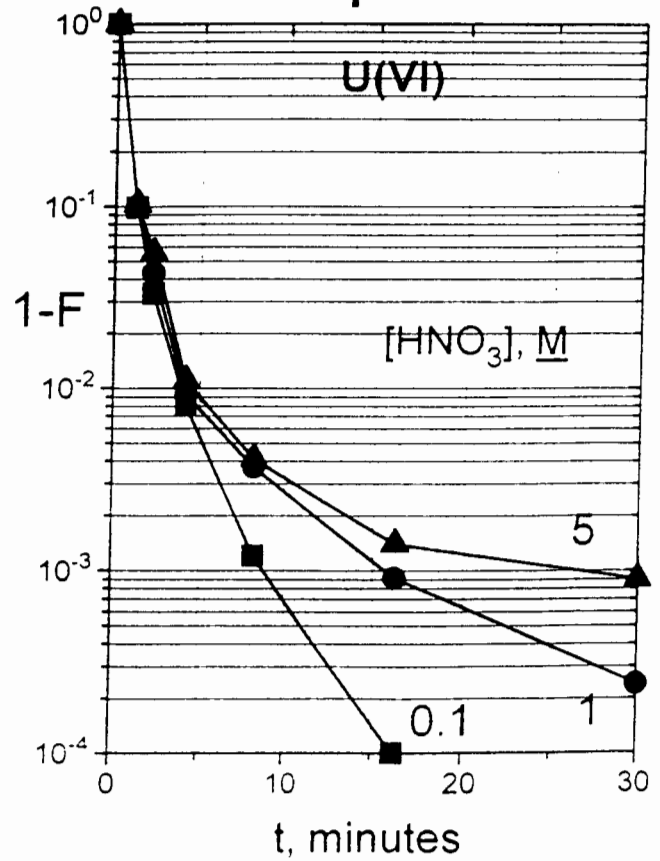
Diphosil



Diphonix



Diphosil



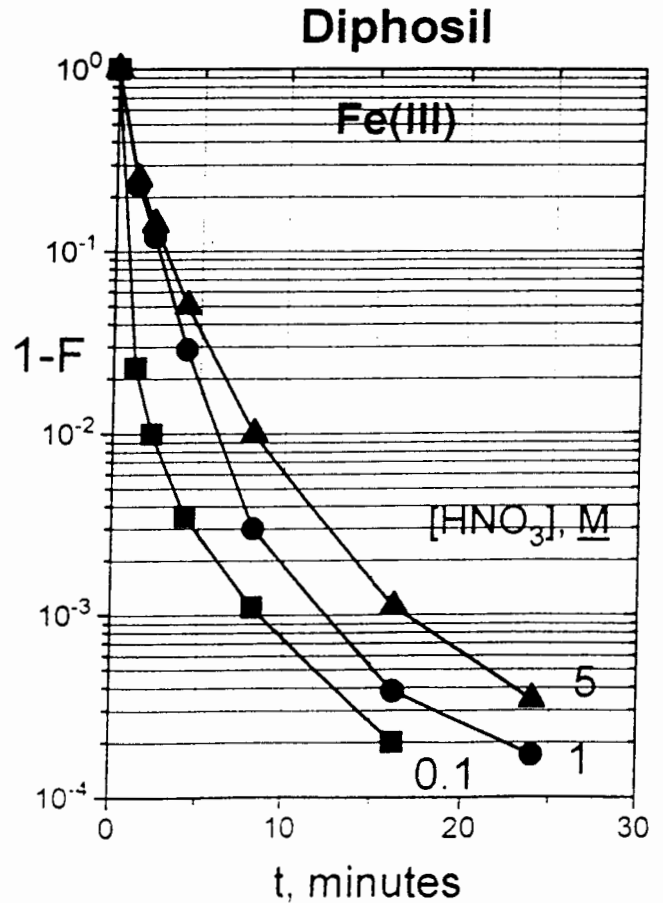
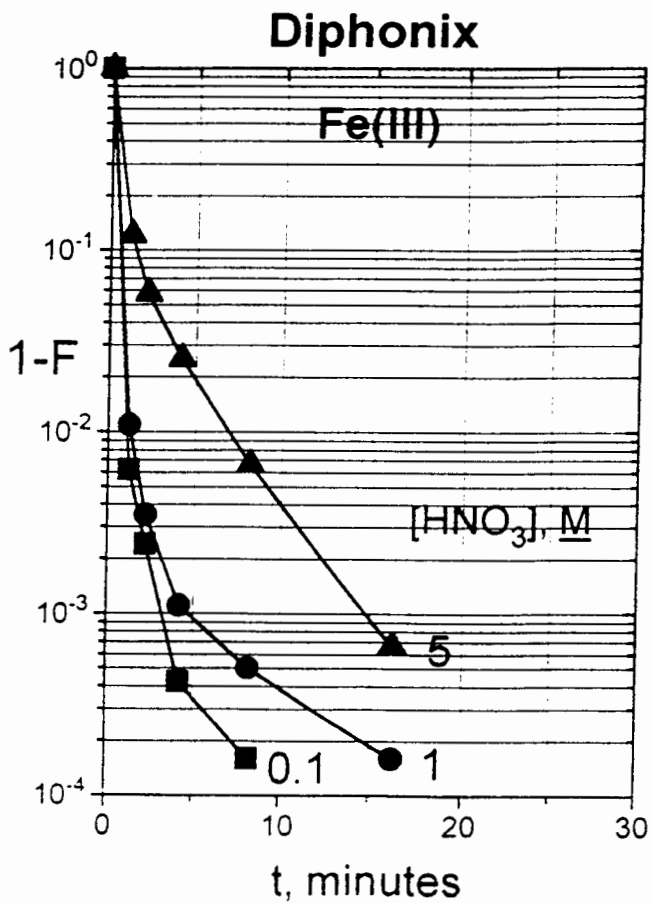
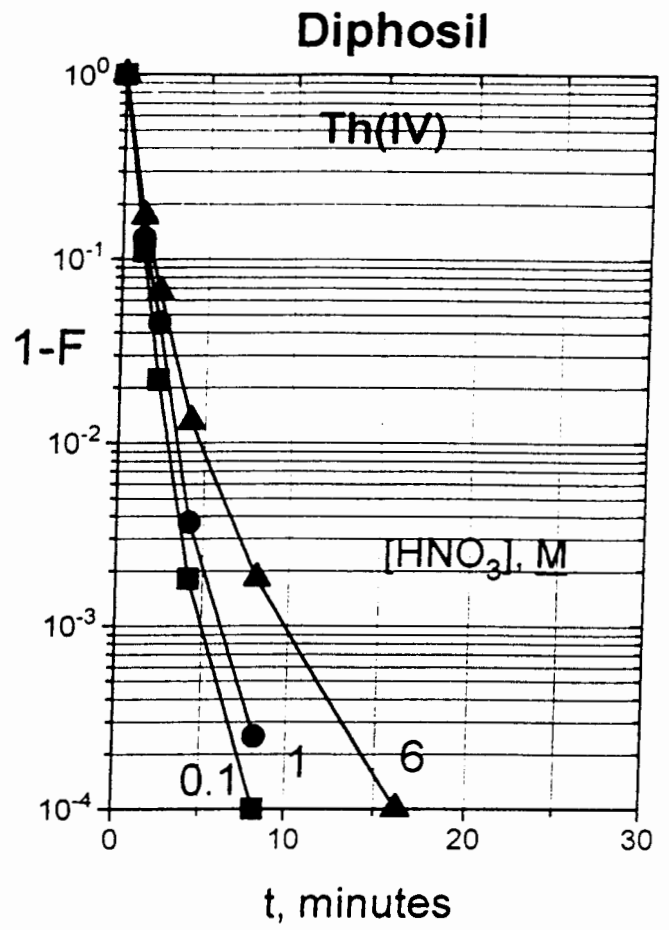
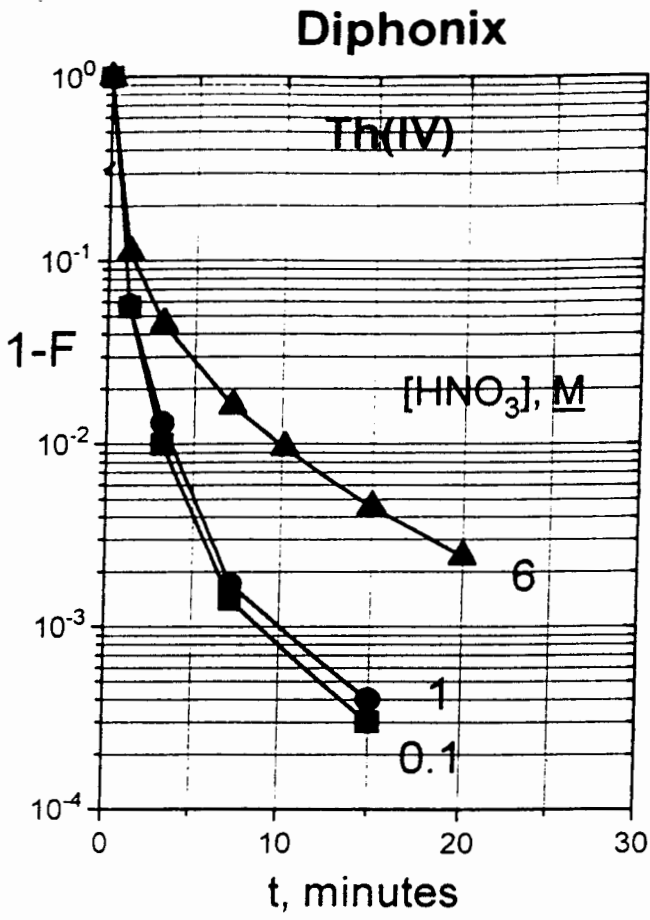


Fig. 9

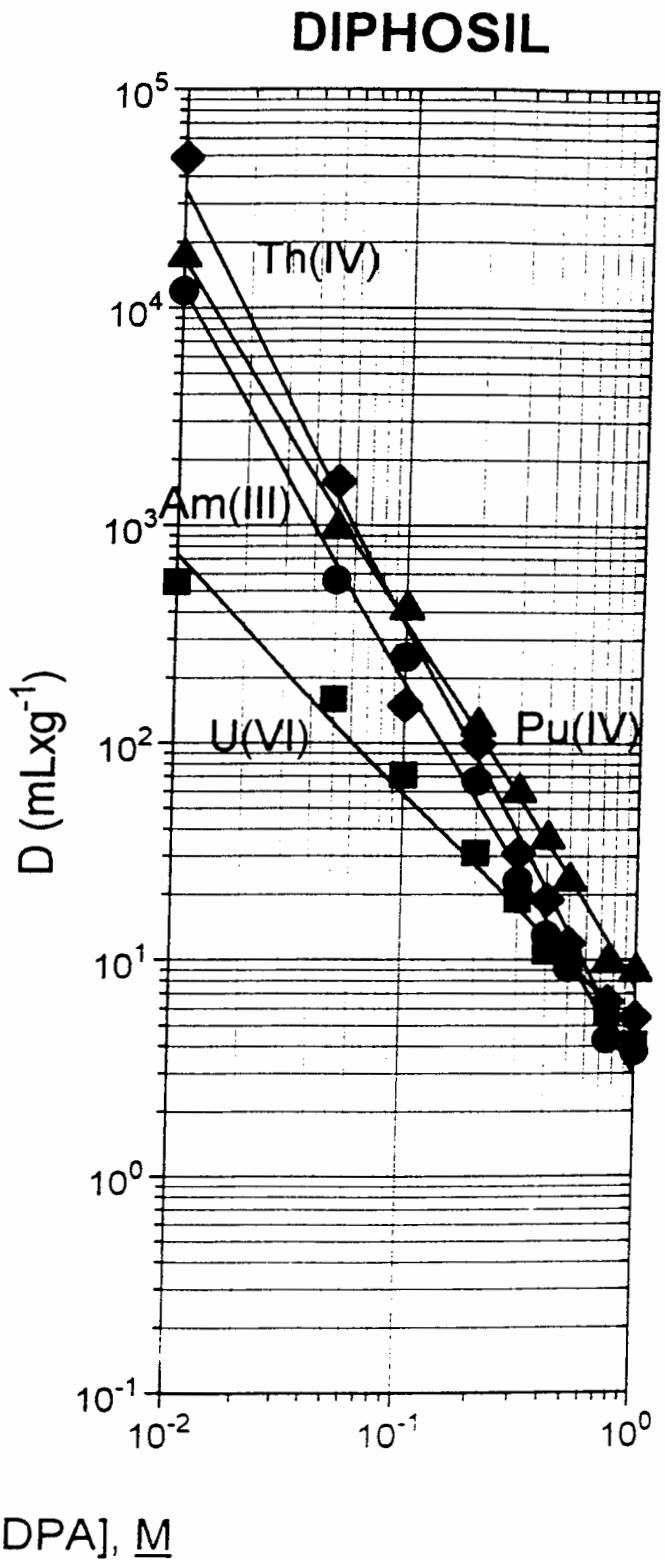
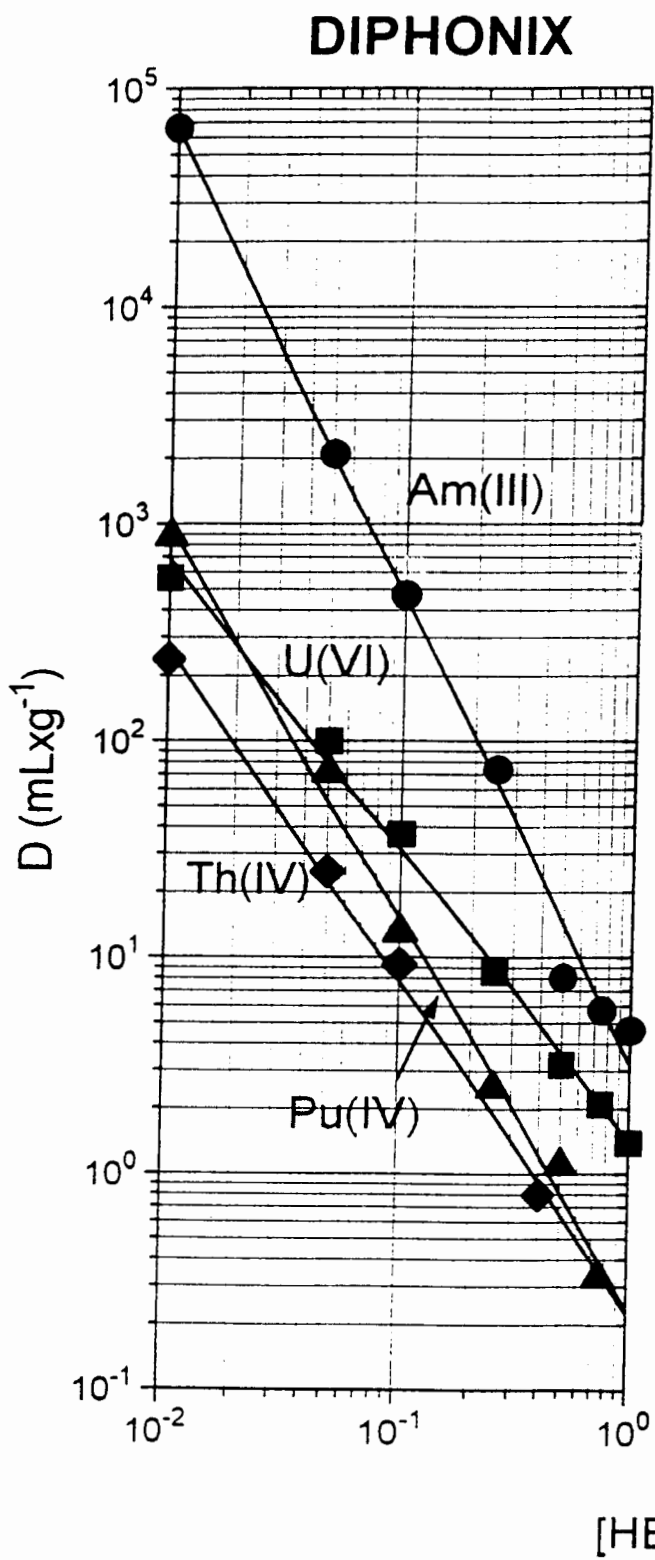


Fig. 10