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DUAL MECHANISM BIFUNCTIONAL POLYMERS FOR THE COMPLEXATION OF LANTHANIDES AND ACTINIDES*

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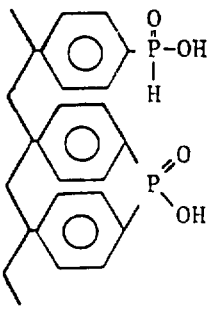
ABSTRACT

Phosphinic acid ion exchange/redox resins are synthesized by the reaction between polystyrene beads and phosphorus trichloride followed by base hydrolysis. The reaction requires a temperature of 73°C for full functionalization to occur. The effect of lower functionalization temperatures on resin acid capacity was determined and the concomitant effect on ion exchange investigated. The acid capacity was found to vary from 1.09 mequiv/g to 4.79 mequiv/g in the functionalization temperature range studied (15°C to 73°C). The percent resin sites loaded with zinc ions is independent of the actual capacity but the time to attain that percent loading increases from 5 minutes to 60 minutes as the absolute amount of zinc loaded increases. The extracting ability of the phosphinic acid resin for europium, thorium, uranium, americium, and plutonium was examined as a function of acid concentration from acid nitrate solutions both at varying and constant ionic strength. The phosphinic resins show better extraction for these ions than the sulfonic resins, especially from high acid solution (4M HNO_3) due to the superior coordination ability of the phosphoryl oxygen. They also show a much higher selectivity for the ions tested over sodium. For example, under conditions where sulfonic resins absorb 53% of the plutonium in solution, the phosphinic acid resins absorb 99%.

INTRODUCTION

Ion exchange resins with an exchangeable proton have been used for the recovery of many metals from solution including iron, copper, zinc, and chromium(1). Both of the most commonly employed cation exchanger types, sulfonic and carboxylic, have been successfully utilized in a number of applications(2), yet both have some important limitations: the strongly acid sulfonic resins tend to be quite non-selective due to facile proton exchange and weak coordination by the sulfonyl oxygens(3) while the weakly acidic carboxylic resins require relatively high pH values for effective exchange(4). We have recently introduced the synthesis of bifunctional phosphinic acid resins(5) and characterized them by their ability to complex zinc ions(6). These resins have been shown to be more selective than the sulfonic acid resins while operating at lower pH values than the carboxylic resins. Additionally, they have been found to operate by a dual mechanism whereby metal ion exchange can be followed by reduction to the free atom if the metal ion has a suitable reduction potential allowing for the isolation of the pure metal from solution(7). Such a redox process has been shown to occur with mercury and silver(7). The bifunctional phosphinic acid resins are thus the first example of what we have termed dual mechanism bifunctional polymers; a second example involving a resin with a dual ion exchange - coordinating mechanism has been prepared(8).

The phosphinic acid resins (I) which have been studied to date are all



(I)

high capacity resins with complete substitution of the polystyrene network by the phosphorus ligands. Complete functionalization is brought about via a high temperature (73°C) reaction between PCl_3 and polystyrene and is important because it minimizes the resin bed volume required to treat a given aqueous stream. On the other hand, the degree of functionalization could be an important control on resin hydrophilicity and, hence, the extent of resin swelling or deswelling in ionic solutions which could, in turn, influence the rate of attrition. Lower degrees of functionalization would lead to lower osmotic forces and thus lower rates of attrition.

This report examines the effect of the functionalization temperature on the resin acid capacity and how the resin acid capacity influences the extent of metal ion complexation at equilibrium and pre-equilibrium times. The ability of phosphinic acid resins to complex europium, thorium, uranium, americium, and plutonium is then examined and compared to the performance of sulfonic acid resins.

RESULTS AND DISCUSSION

Effect of temperature on resin acid capacity

The phosphinic acid resins are prepared by functionalizing polystyrene gel beads with 2% divinylbenzene crosslinking at 73°C with PCl_3 in the presence of 0.77 mole $AlCl_3$ per mol polystyrene using a 4 hour contact time. Subsequent hydrolysis in aqueous base yields polymer with both monoaryl (1°) and diaryl (2°) phosphinic acid ligands. The total acid capacity is obtained by sodium hydroxide titration and confirmed with a phosphorus elemental analysis, while the 1° acid capacity is obtained by an iodine titration of the oxidizable P-H bonds.

The effect of functionalization temperature on both the total and 1° acid capacity is shown in Figure 1. The results clearly indicate that a 15°C

functionalization yields resin with only 1° acid sites; as the reaction temperature increases, the total acid capacity increases but not with a concomitant increase in 1° acid capacity after 25°C. The 1° acid content thus remains constant at 2.3 mequiv/g as the total acid capacity reaches 4.8 mequiv/g, the difference being made up with 2° acid sites(5). With every 20° increase in functionalization temperature, there is an increase of 1 mequiv/g in functionality. We conclude that the synthesis of a high capacity resin requires a reaction temperature of 73°C.

Effect of acid capacity on metal ion complexation

The ability of high capacity phosphinic acid resins to complex Zn(II) ions and to do so more selectively than the sulfonic acid resins in the presence of sodium ions has been well-established(6). The influence of the acid capacity on the percent loading on the resin by Zn(II) ions is given in Table 1. Four resins were examined with different degrees of functionalization: resin A with 1.08 mequiv/g from a 15°C functionalization, resin B with 3.25 mequiv/g from a 30°C functionalization, resin C with 3.90 mequiv/g from a 50°C functionalization, and resin D with 4.79 mequiv/g from a 73°C functionalization. Each was contacted with 0.1, 1.0, and 1.5 milliequivalents Zn(II) ions initially per milliequivalent of resin acid sites in the presence of 20 milliequivalents of sodium ions so as to maintain a constant ionic strength throughout the study. In what follows, the initial ratio of milliequivalents metal ion per milliequivalent acid sites is termed the R_i value. The results show that the equilibrium loading capacity as a percent of the maximum loading possible is independent of the degree of functionalization except for the lowest capacity resin where the resin's hydrophobicity lowers the extent of loading at high salt concentration.

The kinetics of extraction were then established at an R_i of 1. The time to equilibrium was determined for each resin and found to increase in the

order 5 min, 30 min, 45 min, and 60 min for resins A, B, C, and D, respectively. As shown in Table 1, though the percent loading at equilibrium remained constant, the time to equilibrium increased simply because more zinc was being absorbed by the higher capacity resins. As will be shown in a subsequent publication(9), the time to equilibrium for the highest capacity resin can be significantly shortened by making the polystyrene support macroporous(10).

The complexation of lanthanides and actinides by phosphinic acid resins

The removal of metals present in trace quantities from water is important from an environmental standpoint(11) as well as from the standpoint of recovering strategic metals(12). Two important classes of metals whose removal from aqueous streams has been the subject of much research in liquid-liquid extraction are the lanthanides and actinides(13). The excellent performance of the high capacity phosphinic acid resin for recovering metals in these classes, especially when contrasted to the performance of the commonly available sulfonic acid resin, is detailed below.

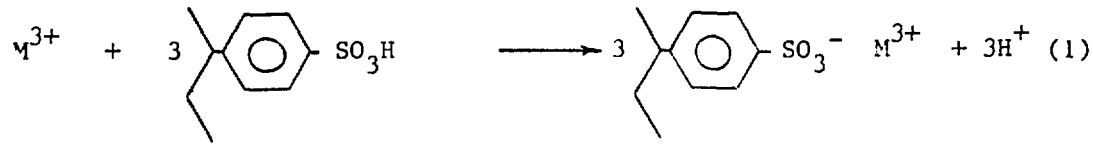
Results are correlated in the usual manner of distribution coefficient, D, vs pH with the corresponding slope calculated(14). The distribution coefficient is defined as the milliequivalents of metal on the resin per gram of resin divided by the milliequivalents of metal in the aqueous solution per milliliter of solution at equilibrium. The distribution coefficient correlations were established in metal ion solutions of varying acid concentration both with nitric acid alone (ranging in concentration from 4M to 0.2M) and with constant nitrate background through the addition of $NaNO_3$. Comparing the results from both cases proved to be instructive about the extraction mechanism dislayed by the phosphinic resins.

Table 1

Effect of resin acid capacity on the extent of Zn(II) complexation

	Resin (mequiv/g)			
	A (1.08)	B (3.25)	C (3.90)	D (4.79)
loading at equilibrium				
R_i = 0.1	5%	5%	5%	5%
R_i = 1.0	27%	25%	31%	27%
R_i = 1.5	24%	32%	42%	46%
time to equil. at R_i = 1.0	5 min	30 min	45 min	60 min
mequiv Zn abs/g at R_i = 1.0	0.27	0.78	1.21	1.29

Europium and Americium The abilities of the phosphinic and sulfonic resins to complex Eu(III) and Am(III) are shown in Figures 2 and 3. While the results for both metals are similar, the behavior of the two resins is strikingly different, especially at constant nitrate concentration. The sulfonic acid resins display classical ion exchange behavior in solutions of varying acidity given that the log D vs pH plots yield a slope of 3.0 for both Eu and Am in the region of pH -0.8 to +0.6 (4M HNO_3 to 0.25M HNO_3). The extraction process is thus represented by equation (1).



(1)

Under the conditions of varying acid solutions, the phosphinic acid resins give a slope of 1.75 for both ions. This is probably due to the extraction of the neutral trinitrate complex (equation (2))

(2)

and the free trivalent cation in the proportion which gives the observed slope. The $M(NO_3)_3$ species is expected to be extracted by coordination with the phosphoryl group in the resin in a manner similar to the extraction of neutral species by tributylphosphate or trioctylphosphine oxide(15). The slope increases only slightly to 1.9 upon performing the exchange at constant nitrate concentration indicating that the previous observations are not an artifact of changing ionic strength. Studying the performance of the resins

at constant nitrate concentration pointed to an important advantage for the phosphinic resins: whereas the phosphinic resins show a significant increase in the M^{3+} distribution coefficient as the acidity is decreased at a constant nitrate background, the sulfonic resins show almost no increase in $D(M^{3+})$ probably due to the competition of sodium ions. The phosphinic resins are thus much more selective for Eu and Am over sodium than is the sulfonic resin which saturates with the sodium that is present in great excess. Perhaps surprisingly, the phosphinic resins also outperform the sulfonic resins in the region of highest acid strength (4M HNO_3) due to a strong coordinative ability which is more important than ion exchange in that acidity region.

Uranium. The conclusions drawn on the performance of the resins with Eu and Am were further confirmed by the extraction of uranium as UO_2^{2+}. The results are presented in Figure 4. The sulfonic resins seem to give a slope of 2 only within the limited pH range of 0 to 0.9; below pH 0, the slope is 0.87 indicating that the coordination mechanism is an important route even for the sulfonic resins in a high acid region. This also accounts for the relatively small effect of the sodium ions on uranium extraction. The phosphinic resins show little dependency on the solution acid strength from 4M HNO_3 to 0.2M HNO_3 (slope = 0.05) thus indicating the operation of a purely coordinative mechanism and a relatively small influence for the constant nitrate background. This mechanism allows the phosphinic resins to be far superior to the sulfonic resins in the region of high acidity: D = 34.8 at 4M HNO_3 for the phosphinic resin vs 2.5 for the sulfonic resin.

Thorium. Results with thorium are summarized in Figure 5. The expected ion exchange process occurs with the sulfonic resin, the observed slope of +3 being due to extraction of the mononitrate as found by Peppard and Mason(16). The presence of sodium ions strongly affects the extent of thorium

absorption by the sulfonic resins, again as expected from an ion exchange process. Interestingly, the phosphinic resins display a coordinative mechanism with thorium as they did with uranium given the insensitivity to pH changes and the presence of sodium ions.

Plutonium. The phosphinic resins regain their decisive advantage when extracting plutonium from constant nitrate solutions as shown in Table 2. The three solutions indicated in the table, which represent a pH range from -0.7 to +0.1, show an eleven-fold increase in the distribution coefficient for the phosphinic resins (6.3 to 70.0) and a 67% decline for the sulfonic resins (3.3 to 1.15).

The results, then, clearly show that the phosphinic resin has great potential for the separation of lanthanide and actinide ions from other ions as well as for the scavenging of these ions from dilute waste streams. Further work is planned to systematically define the extraction characteristics of the resin with other ions.

CONCLUSION

The mechanism by which the phosphinic resins can complex metal ions has been examined and their advantage over the sulfonic resins has been better defined through a study involving a lanthanide and various actinide metal ions. The phosphinic resins complex more metal ions than the sulfonic resins in high acid solution (4M NHO_3) due to a superior coordinating ability and in the presence of sodium ions due to a much greater selectivity.

ACKNOWLEDGEMENTS

We would like to thank Mr. Gerry N. Case (ORNL) and Mr. Paul T. Kaiser (UT) for their help with the radiotracer experiments.

Table 2

Plutonium:

	log D (%abs) at constant NO_3^- background		
	4M HNO_3	1M HNO_3	0.2M HNO_3
	-	3M $NaNO_3$	3.8M $NaNO_3$
Phosphinic Resin	0.797 (86%abs)	1.41 (96%abs)	1.84 (99%abs)
Sulfonic Resin	0.521 (77%abs)	0.29 (66%abs)	0.06 (53%abs)

EXPERIMENTAL

The synthesis of the polystyrene beads and their subsequent functionalization at 73°C has been detailed(5). Temperature was the only variable in the functionalizations presented in the current report: 15°C, 20°C, 25°C, 30°C, 35°C, 40°C, 50°C, and 73°C were the temperatures examined. The total acid capacity of each resin was quantified by a NaOH titration and the primary acid capacity determined by a redox titration with iodine; both procedures have been described previously(5).

Our method for the determination of the resins' equilibrium loading capacity with zinc ions has been published(6). In quantifying the equilibrium loading capacity, a given zinc concentration in 5-mL of aqueous solution was contacted with enough resin to yield 1 milliequivalent of acid sites for a period of 17 h. An amount of zinc stock solution (2 N $Zn(NO_3)_2$ in 2N $NaNO_3$) was used to give initial milliequivalent ratios (R_i) of zinc ions to resin acid sites of 0.1, 1.0, and 1.5; the remainder of the 5-mL solution consisted of 4N $NaNO_3$. Absorption of zinc from solution into the resin was followed by the initial addition of 0.025μC_i ^{65}Zn and subsequent counting of 1-mL samples on a NaI-T&I well-type scintillation counter. Only the 1.1-MeV ^{65}Zn peak was counted. This procedure was extended in determining the kinetics of the extraction process by setting the R_i at 1 and counting after various contact times: 1 min, 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 2 h, 3 h, 4 h, 6 h, and 17 h.

The 17 h contact time was maintained when studying the complexation of europium and the actinides. The resin (enough to yield 1 mequiv acid sites) was contacted with 5-mL of aqueous HNO_3(4M to 0.2M) alone or in the presence of enough $NaNO_3$ in each sample to maintain a constant 4M nitrate background in each solution. Each solution contained radiotracer levels of $^{152-154}Eu$,

^{230}Th, ^{233}U, ^{241}Am, or ^{239}Pu. The only γ-emitter was the Eu and it was counted on the same counter as was the ^{65}Zn. All of the other isotopes were α-emitters and 1-mL aliquots were placed in a scintillating solution and counted on a liquid scintillation counter. A sufficient quantity of each radiotracer was used so that the lowest aqueous sample gave 10,000 counts in a 10 min counting time. This corresponds to a counting accuracy of 1% based on 1 standard deviation. The following peaks were counted for each radiotracer: 0.123-1.4 MeV, Eu; 4.69 MeV, Th; 4.82 MeV, U; 5.57 MeV, Am; and 5.16 MeV, Pu. The amount of radiotracer on the resin was obtained by difference given the blank count rate and the final solution count rate. The distribution coefficient, D for each sample was thus calculated as the counts per minute on the resin per gram of resin divided by the counts per minute in solution per milliliter of solution. The corresponding equilibrium pH of each solution was determined on a Brinkmann pH meter.

Figure Captions

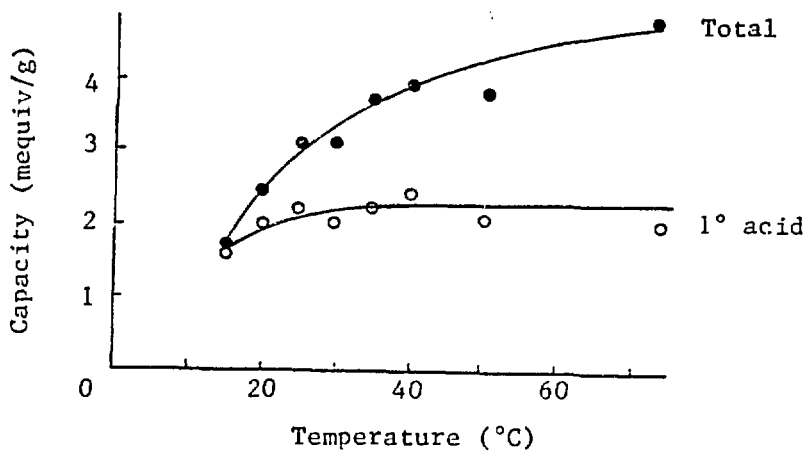
Figure 1. The effect of functionalization temperature on resin acid capacity (mequiv/g).

Figure 2. log D vs pH for Eu(III).

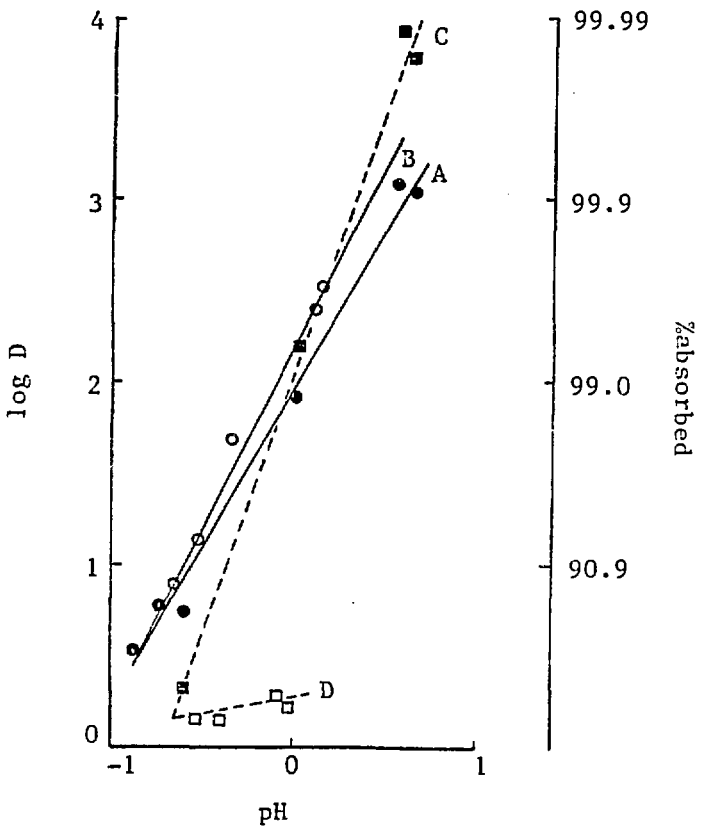
Figure 3. log D vs pH for Am(III).

Figure 4. log D vs pH for UO_2^{2+}.

Figure 5. log D vs pH for Th(IV).


Capacity (mequiv/g)
4
3
2
1
0
20
40
60
Temperature (°C)
Total
1° acid

Europium



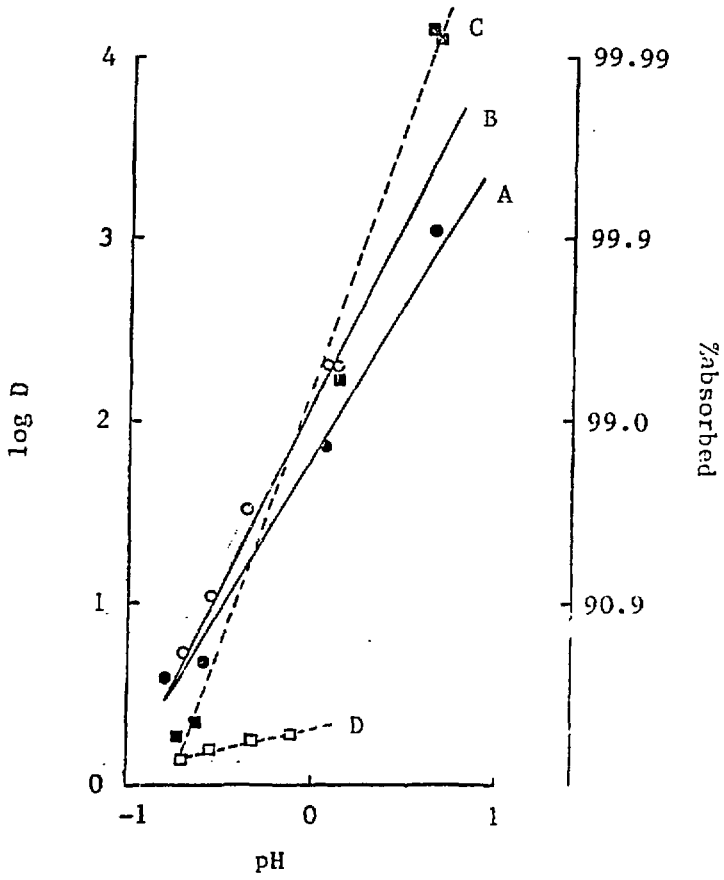
A. Phosphinic acid. Varying HNO_3. Slope = 1.75

B. " Constant $[NO_3^-]$. Slope = 1.90

C. Sulfonic acid. Varying HNO_3. Slope = 3.0

D. " Constant $[NO_3^-]$. (Na exchange)

Americium



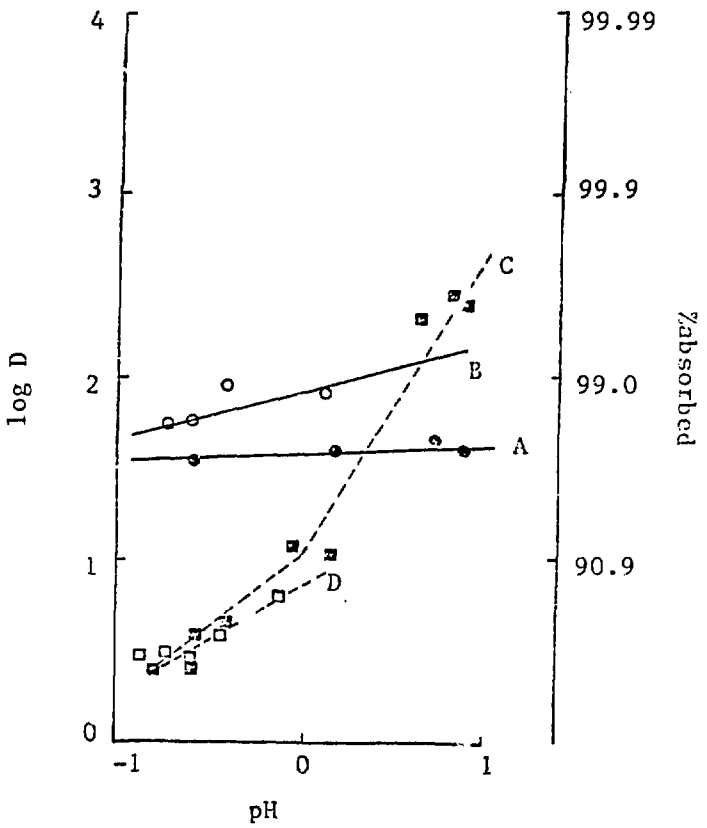
A. Phosphinic acid. Varying HNO_3. Slope = 1.75

B. " Constant $[NO_3^-]$. Slope = 1.97

C. Sulfonic acid. Varying HNO_3. Slope = 3.0

D. " Constant $[NO_3^-]$. (Na exchange)

Uranium (UO_2^{2+})



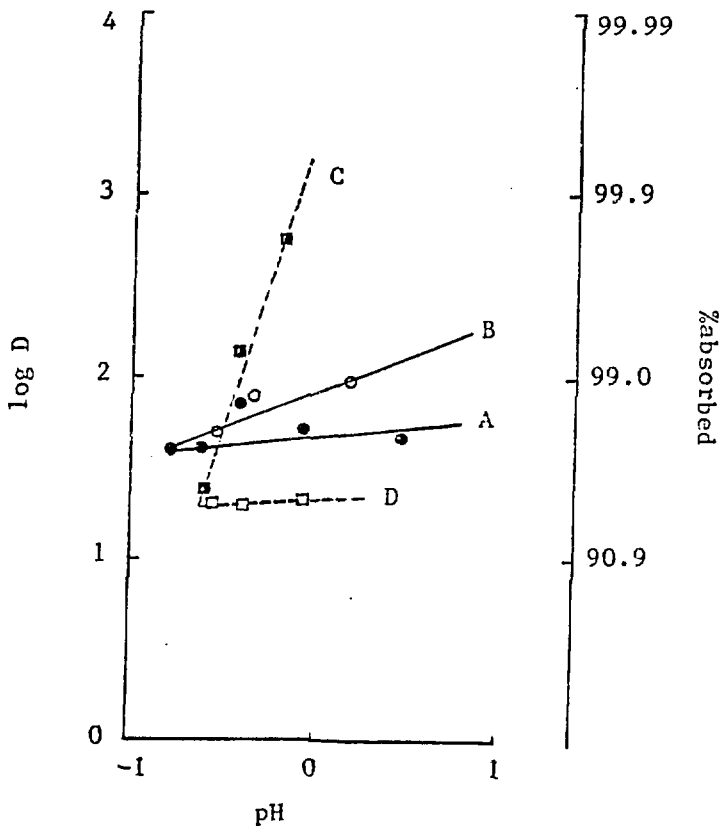
A. Phosphinic acid. Varying HNO_3. Slope = 0.05

B. " Constant $[NO_3^-]$. Slope = 0.19

C. Sulfonic acid. Varying HNO_3. Slope = 0.87 → 2.0

D. " Constant $[NO_3^-]$. Slope = 0.53

Thorium



A. Phosphinic acid. Varying HNO_3. Slope = 0.06

B. " Constant $[NO_3^-]$. Slope = 0.39

C. Sulfonic acid. Varying HNO_3. Slope = 3.1

D. " Constant $[NO_3^-]$. Slope = 0.11

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