Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Gashgari, M. A. , Al-yobi, A. and Ejaz, M.(1990) 'Liquid-Liquid Phase Distribution Studies of Chromium(VI) between Mineral Acid Solutions and 5-(4-Pyridyl)nonane N-Oxide in Benzene, and Enrichment by Extraction Plant with Pulsation Column', Separation Science and Technology, 25: 7, 903 — 920

To link to this Article: DOI: 10.1080/01496399008050373

URL: http://dx.doi.org/10.1080/01496399008050373

SEPARATION SCIENCE AND TECHNOLOGY, 25(7 & 8), 903-920, 1990

Liquid-Liquid Phase Distribution Studies of Chromium(VI) between Mineral Acid Solutions and 5-(4-Pyridyl)nonane *N*-Oxide in Benzene, and Enrichment by Extraction Plant with Pulsation Column

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Abstract

A liquid-liquid extraction system consisting of a benzene solution of 5-(4-pyridyl)nonane *N*-oxide (P_yNO_x) and mineral acid solutions has been studied for the extraction of chromium(VI). The optimal conditions for the extraction have been carefully selected from a critical study of the various factors involved, such as the effects of the concentration of the mineral acids, chromium, and the solvent; and the salting and complexing agents. Common anions have little effect on extraction in concentrations up to 0.5 *M*. Backextraction of the metal can be accomplished by a number of solutions and by water. Extraction of several metals was investigated under optimal conditions for the extraction of chromium. Common base metal ions like iron, aluminum, magnesium, calcium, etc. are not extracted. The mechanism of extraction has been studied by using slope analyses and saturation experiments. The predominant mode of extraction appears to be ionic association with the probable composition of the extracted species being $P_yNO_xH^+ \cdot HCr_2O_7^-$, with some additional contribution by benzene. Extraction at a high aqueous to organic ratio has been studied by using an extraction plant with a pulsation column.

INTRODUCTION

Solvent extraction has become a proven and quite common industrial process for recovering metals from aqueous leach solutions. In such processes, metal ions are partitioned between aqueous leach solutions and water-insoluble organic phases, generally composed of solvents dissolved in organic diluents. Unlike some other metals, chromium is rather difficult to leach directly from its ores which are mostly used in various intermediate forms; e.g., ferrochrome is used directly in steel making. However, in processes such as smelting in a blast furnace or direct reduction to make iron from chromium-containing iron ores, chromium in the concentrate finally goes into a process by-product such as slag. This by-product, when roasted with sodium salts, provides a good source for the leaching of chromium by aqueous solutions of moderate pH's. The leachate solutions can further be subjected to various schemes to isolate chromium from the other elements. Various classes of extractants including carbon and phosphorous-bonded oxygen donors, tertiary and quaternary amines, chelating agents, etc., have been used to extract chromium(VI) from aqueous solutions. These include the extraction of chromium(VI) from hydrochloric acid by methyl isobutyl ketone (MIBK) (*1–3*) and ethyl acetate (*4*). The extraction of chromium(VI) from acid bromide solutions with MIBK is also effective (*5*). It is also good from hydrochloric, nitric, sulfuric, or perchloric acid with tributyl phosphate (*6, 7*) or triphenylphosphine oxide (*8*). High molecular weight amines extract chromium(VI) effectively and have been used for extraction from perchloric, nitric, and phosphoric acids (*9*), and also from sulfuric acid (*10*) and hydrochloric acid (*11*). Since chromium(VI) in weakly acidic solutions is present as large anions, it is also extractable with large cations such as quaternary ammonium salts (*12, 13*). However, most of the reported methods lack efficiency and selectivity of extraction. This report provides original data on distribution studies of chromium in the water–mineral acids–benzene–P_yNO_x system. Distribution, selectivity, and stoichiometric data coupled with high extraction efficiency with large aqueous to organic phase ratios promise to contribute to the development of a scheme to extract and isolate chromium from common base metal ions.

EXPERIMENTAL

Reagents and Equipment

5-(4-Pyridyl)nonane *N*-oxide was prepared by oxidation of 5-(4-pyridyl)nonane according to a procedure reported earlier (*14*). Dilute nitric, hydrochloric, and sulfuric acid solutions were prepared from BDH volumetric solution ampules while the moderate to concentrated acid solutions were prepared by standardization of Merck reagent grade acids. For tracer studies, carrier-free chromium-51 prepared by recoil enrichment (*15*) was used. The carrier used was analyzed grade potassium chromate. Laboratory double-distilled and deionized water was used for the preparation of solutions. The equipment used for radiochemical assay was described in previous reports (*16*).

Distribution Studies

The aqueous phases contained varying proportions of chromium and mineral acids (H_2SO_4, HCl, and HNO_3). The organic phases contained 0.1 *M* P_yNO_x in benzene except for slope-analyses studies where the concentration was varied in the range from 0.1 to 1×10^{-3} *M* in benzene. Phase equilibration was carried out for 5 to 10 min on a shaker followed by centrifugation of the two phases. Prolonged shaking was done for the purpose of convenience, although equilibrium was reached earlier (2 min) and the equilibrium distribution ratio obtained did not change with the additional time. Aliquot portions were then taken from both phases, carefully avoiding any cross-contamination, and were subjected to radiometric assay.

Procedure for Liquid-Liquid Pulsation Column

The pilot plant used in the studies is shown in Fig. 1. Heavy solution (aqueous) from feeding vessel 001 was fed to the top of the column while the lighter phase (organic) was introduced from the bottom. The countercurrent interaction was supplemented by pulsations from the pulsation column. Equilibration was carried out for 10 min, and finally the phases were collected in collecting vessels.

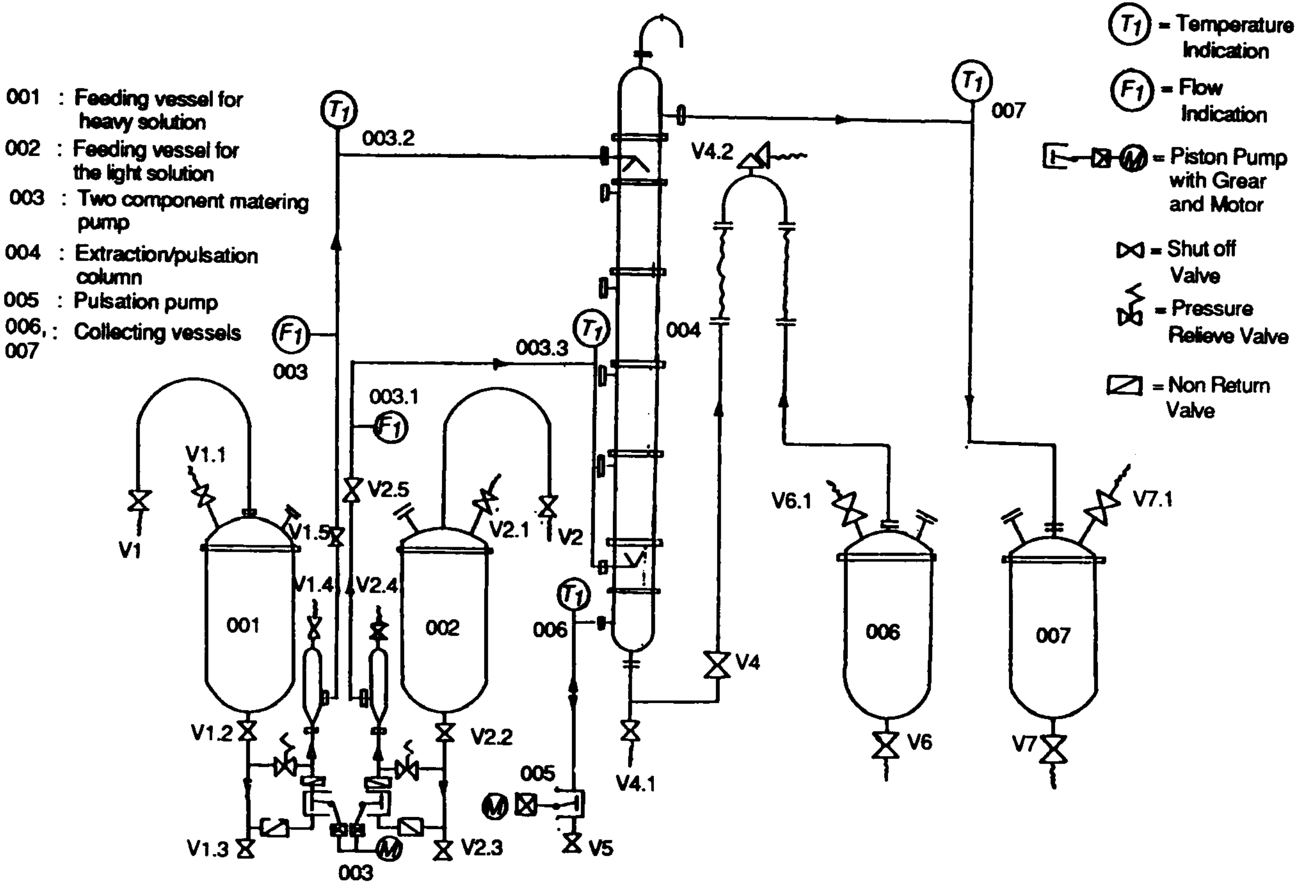

FIG. 1. Liquid–liquid extraction plant with pulsation column.

RESULTS AND DISCUSSION

In preliminary investigations, extraction of trace ($<10^{-6}$ *M*) and macroamounts of chromium(VI) was investigated from sulfuric acid solutions with a concentration range of 10^{-2} to 10 *M* by *N*-oxide of 5-(4-pyridyl)nonane in benzene. The results are shown in Fig. 2. In all the investigated concentrations of chromium(VI), there is an initial increase of *D* with increasing aqueous acid. Obviously this is due to the decreasing activity of water through the formation of thermodynamically stable hydronium ions (ΔH hydration of H^+ ions per mole = -1118.8 kJ). It is seen that $D_{Cr(VI)}$ in very dilute acid solutions is significantly higher for trace concentrations than for relatively higher concentrations, i.e., 0.1 and 1 g/dm^3. A part of the reason could be a rather high solvent to Cr(VI) ratio at trace levels.

Since for trace concentrations of chromium(VI) the concentration of $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ is negligibly small, it is possible that the species of the types $(P_yNO_xH^+)_2 \cdot CrO_4^{2-}$ and $P_yNO_xH^+ \cdot HCrO_4^-$ are extracted through ionic association. These complexes are more likely to exist than the coordination of the *N*-oxide with chromium(VI) in H_2CrO_4. This is because $HCrO_4^-$ associates with hydrogen ions only reluctantly (the formation constant of H_2CrO_4 proceeds with $\log K_{\text{association}} = -1.0$) (*17*). However, the solvation process cannot be ruled out altogether because even if small concentrations of the species (molecular H_2CrO_4) are present, continuous extraction/elimination would be reproducing it again because chemical equilibrium is continuously reestablished.

In the case of relatively higher chromium(VI) concentrations (Curves 2 and 3 in Fig. 2), extraction is small at low acid concentrations. The available H^+ ions concentration is probably not enough to form stable *N*-oxide cations. This is especially so because the increased chromium concentration also tends to decrease hydrogen activity as the equilibrium shifts from chromate to dichromate with the consumption of hydrogen ions and liberation of water molecules. In all three cases, maxima are observed between 10^{-1} to 1 *M*. This is a region where there are maximum free sulfate ions available, and the extraction in these cases could result from high enthalpy changes of aqueous hydration. (ΔH for SO_4^{2-} = -1144 kJ/mol, coupled with the hydration of H^+ ions.)

At higher sulfuric acid acidities, the decrease is apparently due to a stronger bisulfate competition for the oxide cation (the pK_a of the *N*-oxides of this type lies in the 5–5.5 region) rather than the transfer of molecular H_2SO_4 to the organic phase. This is because association of bisulfate with

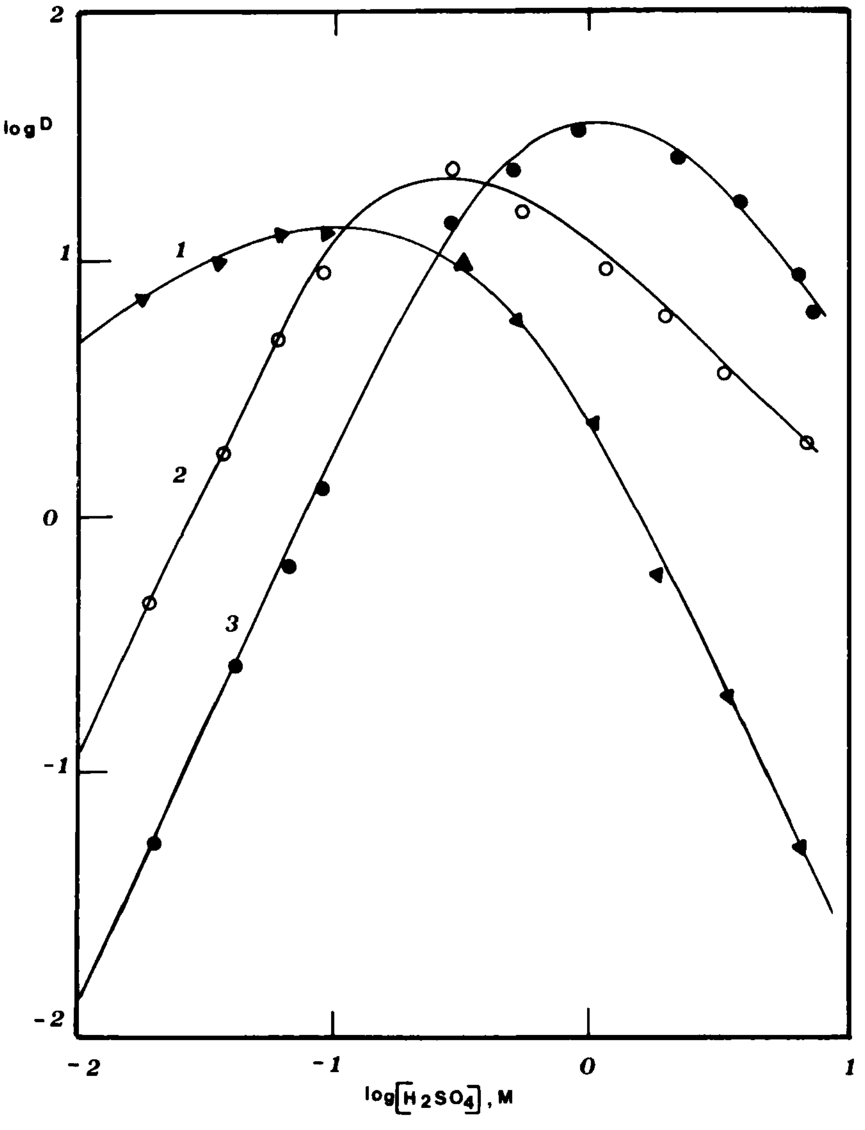

FIG. 2. Variation of distribution coefficient of Cr(VI) between aqueous sulfuric acid solutions and 0.1 *M* P_yNO_x/benzene. (1) Tracer Cr(VI), (2) 0.1 g Cr(VI)/dm^3, (3) 1 g Cr(VI)/dm^3.

the proton in the aqueous phases is very slight even up to fairly high concentrations. This has been supported by Raman spectroscopic results (*18*) and NMR data (*19*) which show that up to 14 *M* the concentration of H_2SO_4 in aqueous solutions is very low.

To elucidate the composition of extractable species in the trace concentration range, variation of the distribution coefficient was investigated with concentrations of the *N*-oxide from constant acidity sulfuric acid solutions of 0.01, 0.5, and 2 *M*. The results are presented in Fig. 3. No clear picture emerges from slope analysis of the plots. This could be the result of the variable nature of the extractable species. In the case of 0.01 *M* acid, the tangent value corresponds to 3.1, in 0.5 *M* acid it has a value of 1.5, while in 2 *M* acid it is lower than 1. Preferential formation and extraction of $H_2Cr_2O_7$ and the association of the oxide bisulfates, which results in micelle formation, could be contributory factors to the low slope from 2 *M* acid. Thus there is no limiting solvation number, although the slope appears to decrease with the acidity of aqueous solutions. The reaction could also result from the increased competition of the supporting acid for the oxide with the subsequent decrease of the association number of the complex metal acid. The reaction can be expressed in Eqs. (1)–(3). However, in these reactions the equilibrium shift of chromium species, which tends to be associated with increasing acid concentration, has been ignored.

$$H_2CrO_4 \cdot 3P_yNO_x + H_2SO_4 \rightarrow H_2CrO_4 \cdot 2P_yNO_x + P_yNO_xH^+ \cdot HSO_4^- \quad (1)$$

$$H_2CrO_4 \cdot 2P_yNO_x + H_2SO_4 \rightarrow H_2CrO_4 \cdot P_yNO_x + P_yNO_xH^+ \cdot HSO_4^- \quad (2)$$

$$H_2CrO_4 \cdot P_yNO_x + H_2SO_4 \rightarrow H^+ + HCrO_4^- + P_yNO_xH^+ \cdot HSO_4^- \quad (3)$$

In the hydrochloric acid system, extractions carried out under conditions similar to sulfuric acid solutions are shown in Fig. 4. The extraction curves, although to some extent similar to the sulfuric acid system, show comparatively lower $D_{Cr(VI)}$. One possibility is the greater affinity of hydrochloric acid for the organic phase, which results from the depressed value of enthalpy changes of aqueous hydration for chloride ions (ΔH_h for $Cl^- = 50.6$ kJ/mol as against ΔH_h for $SO_4^{2-} = -1144$ kJ/mol). Aggregation of free amine *N*-oxide hydrochlorides (especially in the presence of trace

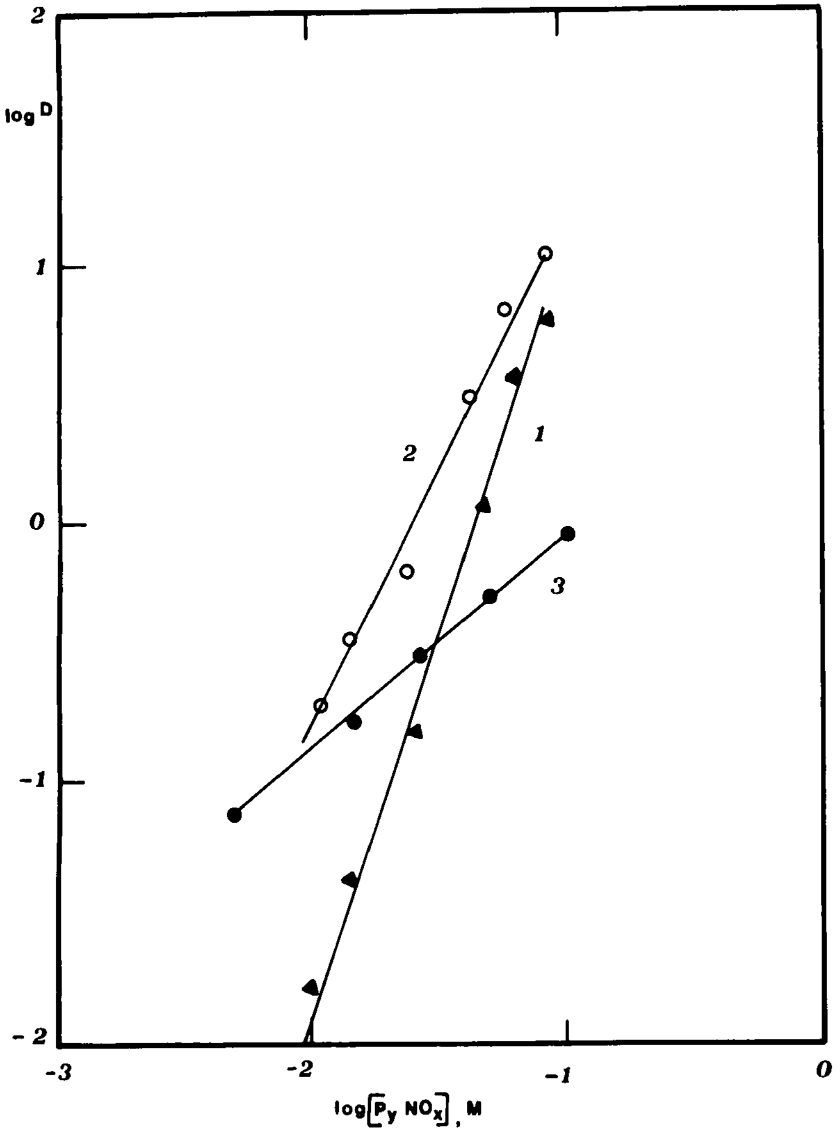

FIG. 3. Effect of P_yNO_x concentration in benzene on the distribution coefficient of Cr(VI) from different concentrations of sulfuric acid solutions. (1) 0.01 *M* H_2SO_4, (2) 0.5 *M* H_2SO_4, (3) 2 *M* H_2SO_4.

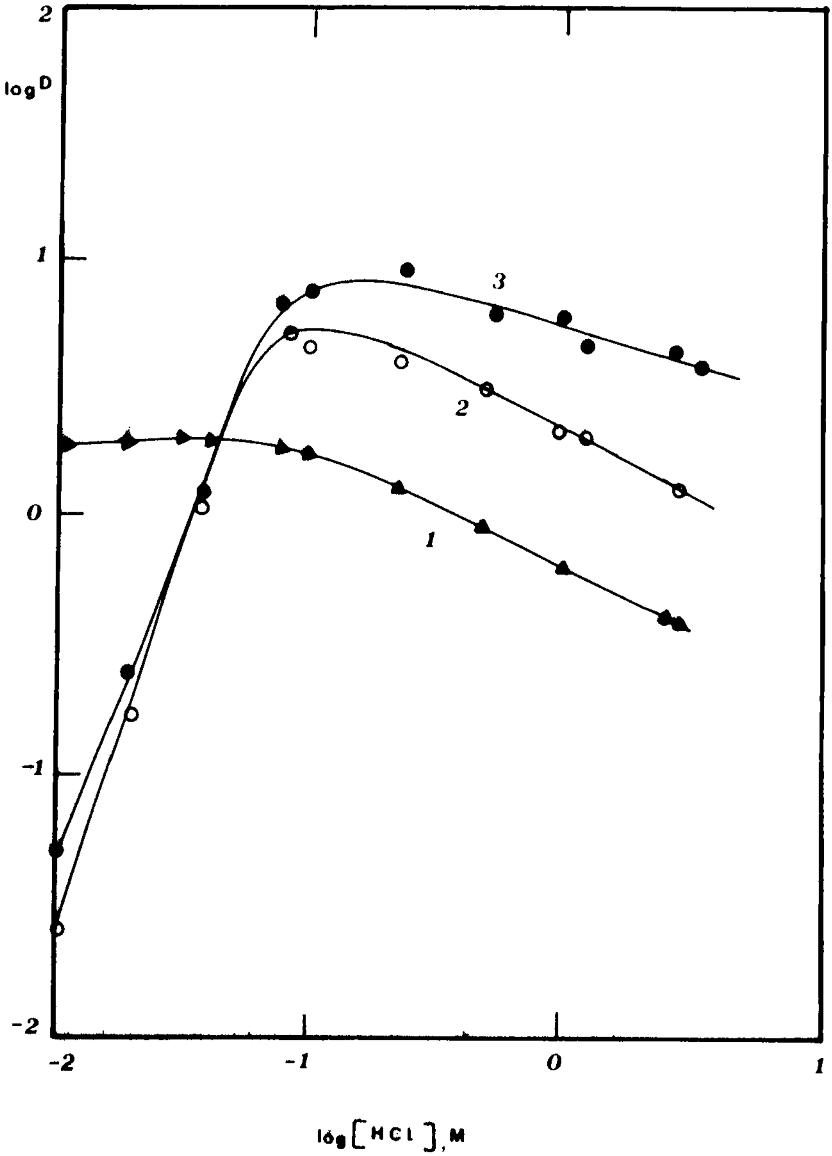

FIG. 4. Variation of distribution coefficient of Cr(VI) between aqueous hydrochloric acid solutions and 0.1 M P_yNO_x in benzene. (1) Tracer Cr(VI), (2) 0.1 g Cr(VI)/dm^3, (3) 1 g Cr(VI)/dm^3.

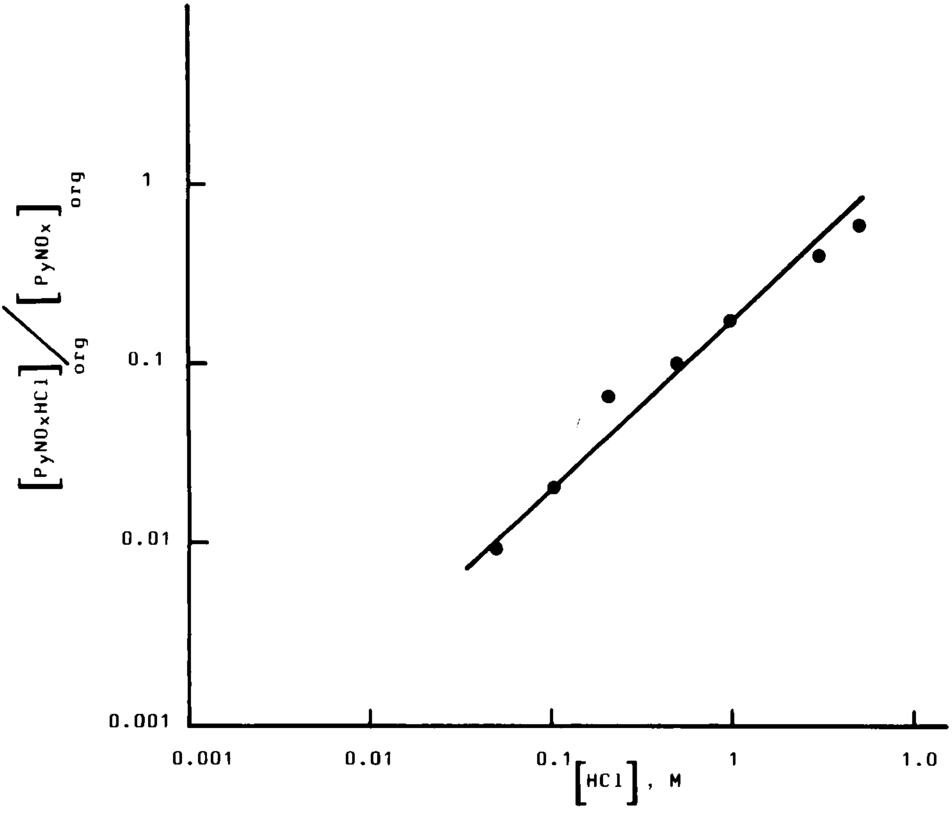

FIG. 5. Plot of log $[(P_yNO_x \cdot HCl)_{org}/(P_yNO_x)_{org}]$ versus log $[HCl]_{aq}$.

metal concentrations) may also contribute to lower *D* values. To check for the possible aggregation, we made use of the extraction data of hydrochloric acid by the *N*-oxide (*14*) and drew a plot of $[P_yNO_x \cdot HCl]_{org}/[P_yNO_x]_{org}$ versus HCl concentration (instead of activities) (Fig. 5), which gave a slope of 1 between 0.5 and 5 *M*. This indicates that a 0.1 *M* benzene solution of the oxide exists in the form of a monomeric species when the acid concentration region is less than 5 *M*. Thus there is no aggregation of the hydrochlorides of the *N*-oxide, at least between 0.5 and 5 *M* acid concentration, although there have been significant polymerizations in the case of pyridine amines (*20*).

The slope-analysis method was again used for the case of hydrochloric acid to find the probable nature of the extractable species of chromium. Because of a loss of activity that was recorded in hydrochloric acid solutions above 0.5 *M*, we confined our investigations to studying the solvent effect from only 0.1 *M* acid. In this investigation, two chromium concentrations were employed, tracer and 0.1 g/dm^3. Slopes of less than 2 were obtained in both cases (Fig. 6).

The studies were also extended to nitric acid media. The region investigated in this case varied from 10^{-2} to 10 *M*. Unlike the other two acids, no reduction of chromium(VI) to chromium(III) was noted in moderate to concentrated acid media.

Plots for the extraction of trace and macroamounts of chromium(VI) in nitric acid media are shown in Fig. 7. The extractions are low in this acid as compared to the other two cases. The apparent reason is the strong competition of nitric acid for the basic oxide. Nitrate ions, being larger and less negative, have a low charge density and are subsequently expected to have lower enthalpies of aqueous hydration and are, therefore, transferred more readily to the organic phase. Though this process, i.e., the transfer of nitrate to the organic solution to give complexes of the $P_yNO_xH^+NO_3^-$ type, leads to lower entropy changes, but the association energies of NO_3^- with the oxide cations, as well as hydration energies of excess hydrogen ions, are large enough to give favorable free-energy changes. The drastic decrease in the extractions at high acidities at all three concentrations is obviously due to competition of molecular nitric acid in the organic phase and subsequent decrease in the concentration of free amine oxide. At lower acidities, perhaps the interaction is not strong enough and the nitrate or the nitric acid is replaced by $HCrO_4^-$ or H_2CrO_4, respectively. In addition to the *N*-oxide, benzene is also known to extract nitric acid through π electrons in a type of hydrate solvate, benzene $\cdot$ $H_2O \cdot HNO_3$, where the intensity of H_2O band in infrared spectroscopy continues to decrease with increasing aqueous acidity (*21*).

Slope-analysis experiments (Fig. 8) carried out from 0.1 *M* nitric acid by 0.1 *M* 5-(4-pyridyl)nonane *N*-oxide gave a slope of nearly 2, indicating the involvement of two solvent molecules per chromium atom. A species of the type $2P_yNO_x \cdot H_2CrO_4$ is most probably the extracted complex.

The contradictory data obtained in slope-analysis studies prompted us to investigate the mechanism of extraction through saturation experiments. Interestingly, not only did a clear picture emerge, but a series of exciting and favorable results was obtained. Figure 9 presents the equilibrium concentrations of chromium in organic and aqueous phases under various extraction conditions. In lower acid concentrations, i.e., 1 *M*, it is

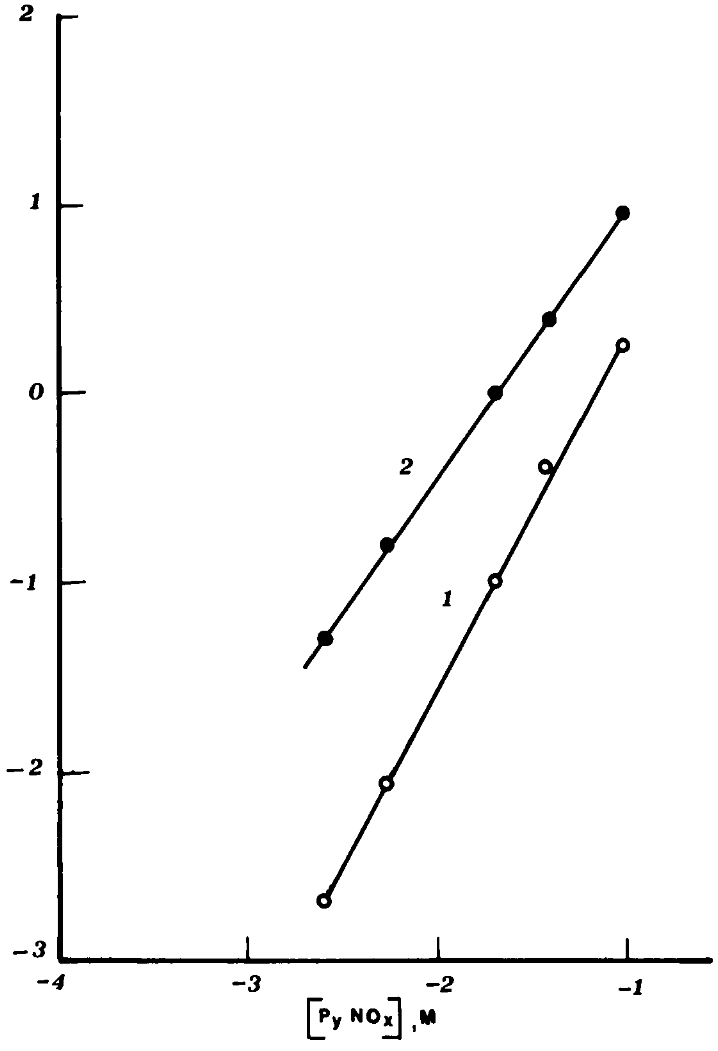

FIG. 6. Effect of P_yNO_x concentration in benzene on the distribution coefficient of Cr(VI) from a 0.1 *M* solution of hydrochloric acid. (1) Tracer Cr(VI), (2) 0.1 g Cr(VI)/dm^3.

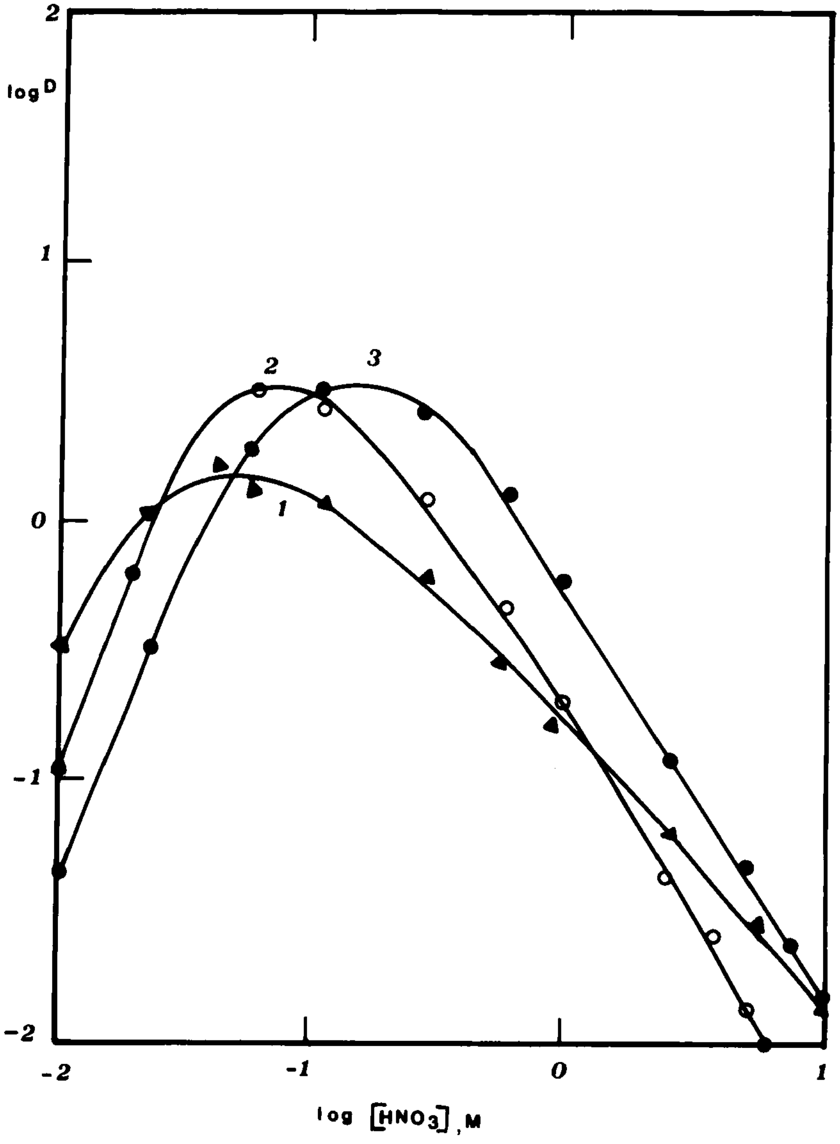

FIG. 7. Variation of distribution coefficient of Cr(VI) between aqueous nitric acid solutions and 0.1 M P_yNO_x in benzene. (1) Tracer Cr(VI), (2) 0.1 g Cr(VI)/dm^3, (3) 1 g Cr(VI)/dm^3.

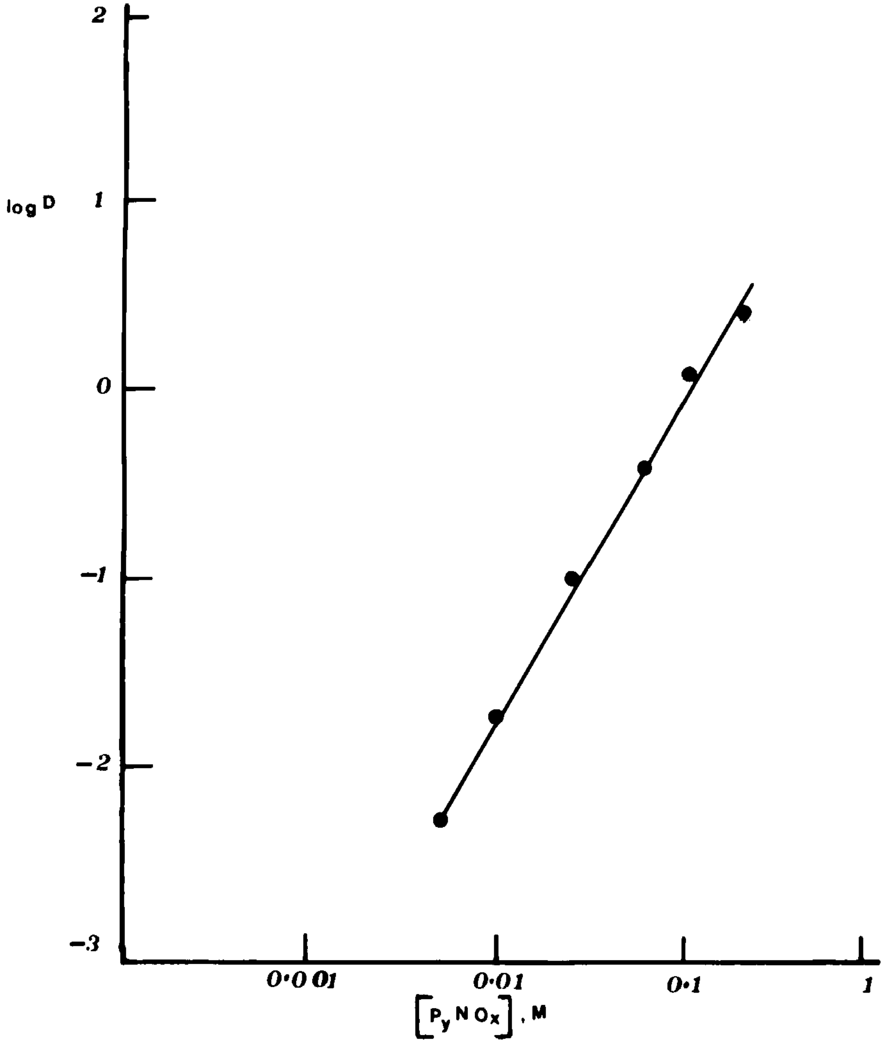

FIG. 8. Effect of P_yNO_x concentration in benzene on the distribution coefficient of tracer Cr(VI) from 0.1 *M* nitric acid.

seen that the loading of chromium in the organic phase decreases as the concentration of chromium(VI) increases in the aqueous phase. The increasing concentration of chromate ions favors the formation of dichromate ions in aqueous solutions. However, this process, as the following reaction indicates, consumes H^+ ions from the aqueous ($2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$) phase. The decreasing concentration of H^+ ions in the aqueous phase probably causes the stability of the oxide cations to decrease in the equilibrium systems, thus favoring the formation of free *N*-oxide. Thus these studies indicate that the predominant mode of extraction is through ionic association rather than by solvation. If it were solvation or coordination of the lone pair of oxygens with the orbitals of chromium, then there would not have been such a significant variation of D on H^+ ions. This explanation sounds logical since loading from higher acid concentrations did not show any decrease with increasing chromium concentrations (Fig. 9). Minor depressions, as can be seen from the figures, could possibly result from statistical deviations in the counting process.

In 3 and 5 *M* sulfuric acid there is an overall increase of chromium uptake with increasing concentration in the aqueous phases. The stoichiometric ratio exceeds the Cr/oxide ratio of 2, which is really very favorable. A complex with a 2:1 chromium–P_yNO_x species can be anticipated to be $P_yNO_xH^+ \cdot HCr_2O_7^-$, but the higher ratio is difficult to explain, especially because chromium(VI) does not form higher polymers as do molybdenum and tungsten. The contribution of benzene toward extraction could be a possibility that needs an independent check, which we have not made.

Selectivity measurements were carried out on a series of elements from 3 *M* sulfuric acid by a 0.1 *M* solution of 5-(4-pyridyl)nonane *N*-oxide in benzene. Special emphasis was placed on the base elements, fission products, and the elements found in a nuclear reactor's coolant water due to the corrosion of structural components. The results are shown in Table 1. The measurements were mostly carried out with radioisotopes of the corresponding elements, especially those which could easily be prepared by neutron activation. Atomic absorption spectrometry was employed in some cases.

Among the alkali metals, no extraction was observed when cesium was tested. This is due to the absence of empty p and d orbitals, and thus a lack of complex formation. From the alkali metals which are also poor complex formers, calcium, magnesium, and barium were examined, and again no extraction was recorded. From the trivalent elements, aluminum was not extracted at all. This is because of its very high hydration enthalpy

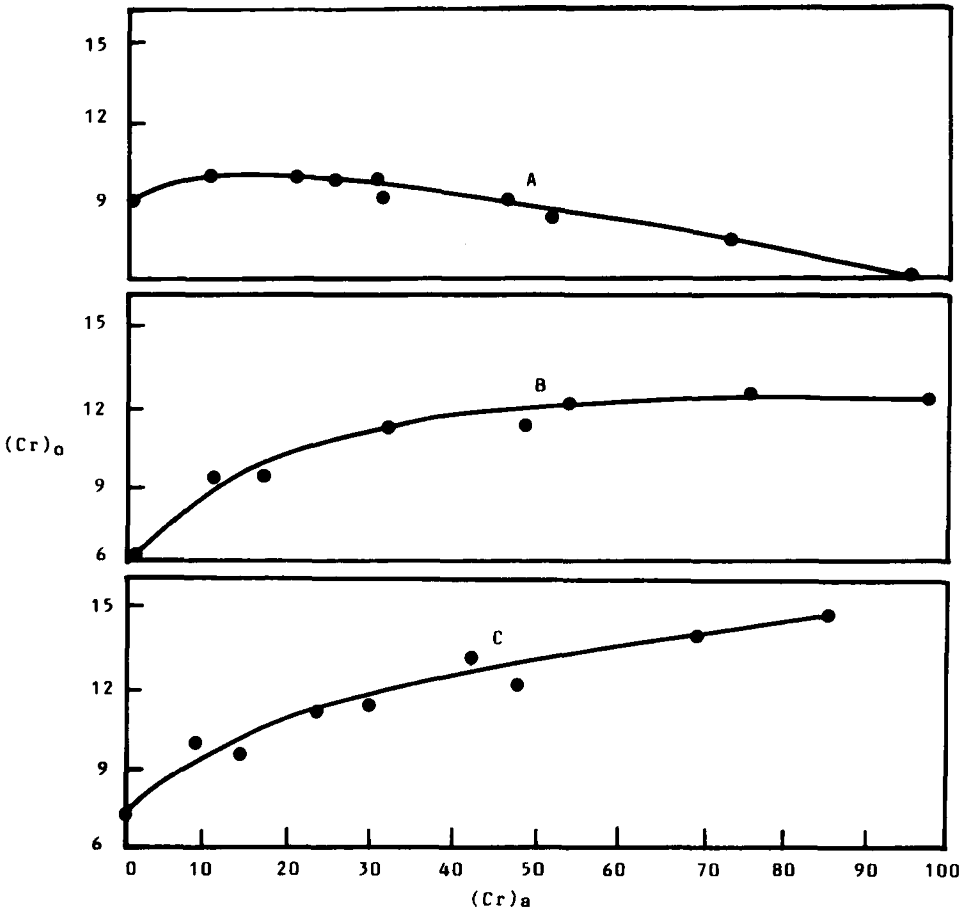

FIG. 9. Equilibrium distribution of Cr(VI) between aqueous sulfuric acid solutions and 0.1 *M* benzene solution of 5-(4-pyridyl)nonane *N*-oxide. (A) 1 *M* H_2SO_4, (B) 3 *M* H_2SO_4, (C) 5 *M* H_2SO_4.

TABLE 1
Distribution Coefficients of Various Metal Ions between 0.1 *M* 5-(4-Pyridyl)nonane *N*-Oxide in Benzene and 3 *M* Sulfuric Acid

Metal ion	Concentration (<*M*)	Distribution coefficient	Separation factor
Cr(VI)	2×10^{-2}	25	—
Cs^+	10^{-8}	0.00	$>10^3$
Ba^{2+}	10^{-8}	0.00	$>10^3$
Ca^{2+}	10^{-5}	0.00	$>10^3$
Mg^{2+}	10^{-4}	0.00	$>10^3$
Co^{2+}	10^{-7}	0.00	$>10^3$
Cd^{2+}	10^{-9}	0.00	$>10^3$
Fe^{3+}	10^{-5}	0.00	$>10^3$
Al^{3+}	10^{-6}	0.00	$>10^3$
Zr(IV)	10^{-8}	0.00	$>10^3$
Nb(V)	C.F.[a]	0.82	0.03
Mo(VI)	C.F.	0.03	$>10^2$

[a] C.F. = Carrier-free.

which results in strong aqueous sheaths which protect it from common complexing agents. The distribution coefficients of some elements, including molybdenum and some other fission products, are shown in Table 1.

The effect of common salts, i.e., sodium sulfate, sodium nitrate, and sodium chloride, was investigated from the corresponding acid solutions. The acidities used were the same as where the maxima were recorded. In sulfuric acid it was 1 *M* (1 g Cr(VI)/dm^3), while in hydrochloric and nitric acid the concentration was 0.1 *M*. In all three cases the addition of the corresponding salt did not have any significant effect on the distribution coeffficient.

Masking studies were made with several anions, especially those which act as bases in aqueous solutions. These included citrate, tartrate, oxalate, and phosphate ions. With trace concentrations of Cr(VI), all these ions backextracted chromium from the organic phase when their concentration in 3 *M* H_2SO_4 exceeded 0.1 *M*.

Finally, 3 *M* sulfuric acid containing 2 g chromium/L was equilibrated with a 0.1 *M* solution of 5-(4-pyridyl)nonane *N*-oxide in benzene using 10 to 1 volume ratios in a liquid-liquid extraction plant (aqueous 50 L and organic 5 L). The concentration of chromium in the organic phase amounted to 12.5 g/L, which is very close to the maximum loading recorded by 1:1 volume ratio studies while using much larger aqueous volumes. This indicates that the procedure cannot only be used for the selective isolation of chromium from base metal ions, but could also be used as a preconcentration step in certain analytical measurements.

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Received by editor May 12, 1989