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Extraction Separation Studies of Gold by 2-Hexylpyridine

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Abstract

The high molecular weight pyridine amine, 2-hexylpyridine, has been studied as a component of solvent extraction systems. Extraction of mineral acids by the compound is described. The ionization constant (pK_{BH^+}) has been determined by potentiometric titration and spectrophotometrically. The distribution of Au(III) between solutions of 2-hexylpyridine in benzene and different mineral acid solutions has been investigated as a function of the concentration of the acids, extractant, and salting-out agents. The extraction mechanism and the composition of extracted complexes of Au(III) are discussed. Separation factors of a number of metal ions relative to gold have been reported, and the determination of gold from a number of synthetic and ore samples was made by neutron activation analysis. 2-Hexylpyridine has been shown as a selective extraction reagent for gold. It has been shown that 2-hexylpyridine dissolved in benzene will extract gold efficiently and reversibly from moderate acid chloride, nitrate, and sulfate media, and that among the common anions only neutral chloride exerts a slight depressing effect on extraction when present in high concentration. The presence of ferric iron does not interfere with extraction.

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INTRODUCTION

In connection with investigations of the extraction ability of high molecular weight pyridine amines, we had earlier investigated (*1–7*) extraction of various metal ions from different mineral acid solutions using symmetrical 4-(5-nonyl)pyridine (NPy) which has proved to be a potential extractant for many metal ions. This communication presents recent fundamental and applied studies on the extraction of gold from different mineral acid solutions by another high molecular weight pyridine amine, 2-hexylpyridine (HPy). This reagent like NPy has been found to form salts with many acidic materials and may be termed, accordingly, "liquid anion exchanger." As such it exhibits selectivities for simple inorganic ions which are qualitatively similar to conventional ion exchangers, i.e., preference for large, poorly hydrated ions (*8*). The trend of selectivity of the extraction process was successfully correlated (*8*) with the degree of hydration of the anion, which is, in turn, a function of its size. Large, single-charged ones, such as perchlorate, apparently without a primary hydration shell in aqueous solutions, extract readily with the equally unhydrated pyridine cations. Smaller simple anions show decreased extractability. This phenomenon makes the liquid systems of some potential interest as a means of separation of inorganic anions. As compared to pyridine and its methyl-substituted derivatives, this amine, like NPy, gives very clean phase separations in acid solutions which cannot be obtained by the lower members of the series. However, this pyridine, unlike the parent molecule (*9*), does not extract septivalent metal oxyanions from alkaline solutions. This is possibly because the lower members have comparatively less electron density at the active nitrogen atom and a greater tendency for hydrogen bonding with water, which possibly leads to a hydration solvation type of mechanism in the extraction of oxyanions of rhenium, manganese, etc. This probably does not occur in the case of HPy because of its comparatively higher electron-donor properties due to the inductive effect of the attached hexyl chain which favors electrostatic bonding and inhibits hydrogen bonding. In this respect the behavior of this amine is similar to NPy.

EXPERIMENTAL

Reagents and Nuclides

2-Hexylpyridine (K & K Labs., Plainview, New York) was used without preliminary purification. It is a pale yellow oily liquid and has a distillation range of 203 to 208°C and d^{20} 0.8959/cm^3. It does not have the very pungent odor which is characteristic of the lower members of the series, but unlike NPy it does have an odor similar to that of green peppers. Mineral acid solutions were generally prepared from B.D.H. volumetric solution ampules or were of Merck "Pro analysis" grade; their solutions were standardized against solutions of sodium hydroxide of appropriate concentrations. NaOH solutions were freed from carbonate by preparing a standard solution of the alkali and passing through De acedite FF(OH^-) form before dilution to the required volume. Standardization of the alkali solutions was done against *N*/5 potassium hydrogen phthalate solution prepared from the "primary standard" grade sample of the salt after drying it at 110°C for 3 hr. $^{198+199}$Au was obtained by neutron activation of spec-pure gold foil (>99.9% purity) in the irradiation facilities of the swimming pool nuclear reactor PARR-1 of this institute. It was dissolved in aqua regia and taken up in different acid solutions by repeated evaporation with the corresponding acids. Care was taken not to evaporate to dryness because appreciable loss of gold can occur when this happens (*10*). ^{233}U was purified by solvent extraction (*11*) before use (the concentration of uranium in the initial aqueous phases was $< 10^{-3}$ *M*). ^{234}Th and ^{230}Th with a ^{230}Th:^{232}Th ratio of approximately 0.085 were isolated from an old sample of uranyl chloride (*12*) and a pitchblende mineral sample (*13*), respectively. ^{99m}Tc was separated from its parent 66.6-hr ^{99}Mo by solvent extraction according to the method of Faddeeva et al. (*14*). ^{51}Cr, ^{64}Cu, and ^{99}Mo were obtained by neutron activation of the respective reagent grade salts, K_2CrO_4, CuO, and MoO_3. The radioisotopes ^{60}Co, ^{59}Fe(III), ^{54}Mn, ^{63}Ni, and ^{144}Ce in chloride form; ^{95}Nb and ^{95}Zr (freed from its daughter ^{95}Nb before use) in the form of oxalate complexes in oxalic acid; and ^{110m}Ag in nitric acid solution were obtained from Radiochemical Centre, Amersham, England, and were pure enough to meet the catalog specifications. The radiochemical purity of the tracers was checked in all cases by γ-ray spectrometry and some times by β-ray absorption plots.

Radiochemical Assay and Instrumentation

For α-assay an argon-flow proportional counter, Harwell type 3–7/11558 in conjunction with an ECKO fast scaler type N 530 F, was used and also a Nuclear Chicago Corporation α-scintillation counter Model DS-S Serial 1709. Solid β-emitting samples were assayed with an end-window Geiger assembly equipped with a G.E.C. tube type EHM 2-S. γ-Ray count rates were determined with a Nuclear Chicago single-channel analyzer, model

872, coupled with a 3 × 3 in. NaI(Tl) well-type scintillation counter. γ-Spectra were taken with a Nuclear Data ND-4410 computer system 512–1024 multichannel analyzer model 2560. The detector used with this analyzer was a 4 × 3 in. NaI(Tl) crystal. The titrations were done on the Fisher titrimeter Model-36, manually for better control near the end point. Optical density measurements were done on a Backman DU Spectrophotometer, whereas the spectra were recorded on a Cary-15 Recording Spectrophotometer.

Procedure for the Extraction of Mineral Acids

One milliliter of 0.1 *M* solution of HPy in benzene was pipetted into a shaking bottle fitted with an air-tight stopper. To this was added 1 ml of the aqueous acid solution of appropriate molarity and the stoppered bottle was mechanically shaken for 3 min to effect equilibration between the organic and aqueous phases. Phase separation was done through centrifugation and 500 μl of the aqueous phase was accurately pipetted out and titrated potentiometrically against a standard alkali using a calomel–glass electrode pair. In titrating strong acids against the standard, the titrant was added to the pH 7 value and the volume of the alkali solution required was noted. The amount of acid taken up by the organic phase was calculated as the difference of the initial and final concentrations in the aqueous phase. All experiments were done at room temperature, 23 ± 2°C. Data reported are an average of duplicate runs.

Determination of pK_{BH^+} Value of the Pyridine by Potentiometric Method

pK_{BH^+} was determined in 10, 20 and 30 wt-% alcohols. For the 10 wt-% alcohol–water mixture, 25 μl of HPy were dissolved in 50 ml of this mixture, and this solution with 2.73×10^{-3} *M* concentration was titrated with 0.105 *N* $HClO_4$. For the 20 wt-% ethanol–water mixture, 50 μl of HPy were dissolved in 50 ml of this mixture, and this solution with 5.46×10^{-3} *M* concentration was titrated with 0.105 *N* $HClO_4$. For the 30 wt-% ethanol–water mixture, 50 μl of HPy were dissolved in 50 ml of this mixture and this solution with 5.46×10^{-3} *M* concentration was titrated with 0.105 *N* $HClO_4$. In pure water the concentration of HPy in 50 ml solution which was titrated with 0.105 *N* $HClO_4$ was 2.184×10^{-3} *M*. Acid was added with a 100 μl syringe. A Fisher expanded scale pH meter with pH readable to ±0.01 was used. The instrument was calibrated by buffers with pH 7.0 and 4.0, respectively. The pK was determined by

$$\mathrm{p}K = \mathrm{pH} + \log \frac{[\mathrm{BH}^+] - [\mathrm{H}^+]}{[\mathrm{B}] + [\mathrm{H}^+]}$$

in which the correction for hydrogen ion was applied to the pK determined from the above equation. The activity correction was applied by

$$\mathrm{p}K_a{}^T = \mathrm{p}K_a{}^M \pm \frac{0.505\sqrt{I}}{1 + 1.6\sqrt{I}}$$

where the plus sign was used for acids and the minus sign was used for bases, and I is the ionic concentration.

Determination of pK_{BH^+} Value of the Pyridine by Spectrophotometry

Hexylpyridine cation (HPyH$^+$) gave a good absorption maximum in 0.01 M HCl at an analytical wavelength of 263.5 nm, and the free pyridine also absorbs at the same wavelength with an absorption of less than 50% of that of the cation. To find the absorption of the mixture of ion and the molecule, a series of buffers (10^{-2} M CH_3COOH + 10^{-2} M KH_2PO_4 + KOH) were prepared to adjust the pH, and the OD was measured for various sets of [BH$^+$]/[B] ratios using a buffer solution of identical composition and pH as the blank. The pK was calculated by

$$\mathrm{p}K = \mathrm{pH} + \log \frac{d - dm}{d_I - d}$$

where d_I is the optical density of the ionic form of the pyridine for the analytical wavelength and dm is the OD of the molecular form.

Determination of D values

All of the experiments were carried out at room temperature (23 ± 2°C). The concentration of Au(III) in the original aqueous phases was $< 10^{-7}$ mole/l. Equal volumes (2 ml) of an aqueous solution and of benzene containing 0.1 M HPy (preequilibrated with the excess of the aqueous phase) were placed in a stoppered glass tube, and the two phases were agitated mechanically for 5 min (sufficient time for equilibration) and centrifuged. The γ-radioactivity of the samples from both phases was measured with a well-type scintillation counter (NaI). The distribution ratio of gold was obtained by

$$\frac{\mathrm{Au(III)_{org}}}{\mathrm{Au(III)_{aq}}} = \frac{\gamma\text{-count rate per ml organic phase}}{\gamma\text{-count rate per ml aqueous phase}}$$

The distribution coefficients of other γ-emitter nuclides were determined similarly, while the procedures for α- and β-emitters are described elsewhere (*15*).

RESULTS AND DISCUSSION

The extraction of nitric, hydrochloric, and sulfuric acids by HPy was studied because the acid extraction equilibria are inherently fundamental to all other equilibria involving the pyridine salts. The results are shown in Fig. 1 in which the aqueous acid concentration is plotted against the fraction* of the pyridine in hydrochloride, nitrate, and sulfate forms. These are essentially titration curves of the base form with acid. Nitric acid is extracted more than hydrochloric acid, and hydrochloric acid extracts better than sulfuric acid. This mirrors the increasing importance of the charge, size, and hydration of the anions of these acids in the aqueous phase. Figure 1 shows that the amine is not completely in the salt form even when the concentration of original aqueous acid solutions is close to 2 *M*, indicating that it is significantly less basic than aliphatic amines. The $\mathrm{p}K_{\mathrm{BH^+}}$ value of the compound was determined by potentiometric titrations. The value of the acid p*K* of the pyridine in water was found to be 6.07 ± 0.7. An estimate was also made by extrapolation of the p*K* value in different wt-% of alcohol in water as solvent to 0% alcohol, and the value was found to be 6.11 ± 0.05. Although the extrapolation from the points obtained with 10, 20, and 30 wt-% alcohol was very nearly a straight line, there is always an uncertainty of a change in behavior between the last experimentally determined point and the % intercept, and it is considered advisable to augment this data through spectrophotometric determination of the p*K*. The UV absorption spectra of the molecular and the cationic form of the pyridine are shown in Fig. 2, and a typical set of data is presented in Table 1. The ionization constant of $\mathrm{HPyH^+}$ as determined spectrophotometrically was found to have a value of 5.94 ± 0.05 at 25°C.

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*Fraction is the ratio in moles of the amine in acid form to that of total amines (0.1 *M*) in the organic phase.

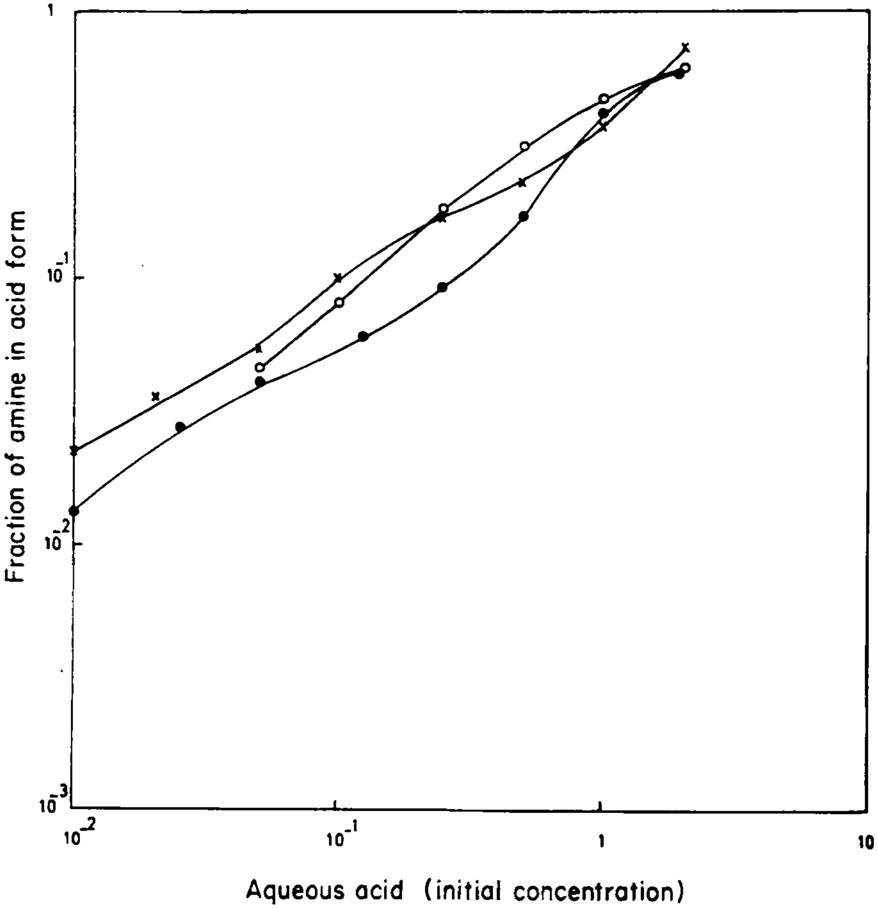

FIG. 1. Effect of acid concentration on the extractant form, organic phase = 0.1 *M* HPy/benzene: (○) HNO_3, (×) HCl (●) H_2SO_4.

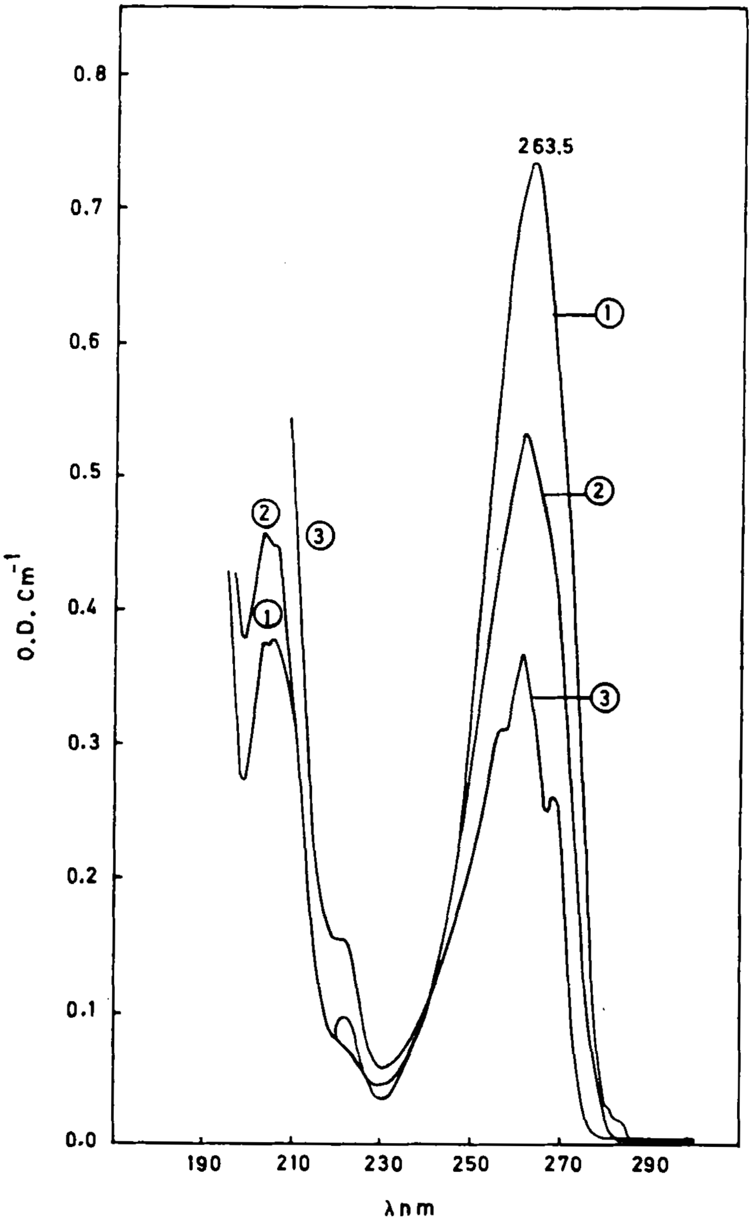

FIG. 2. Absorption spectra of 8.7×10^{-5} *M* hexylpyridine in (1) 0.01 *M* HCl, (2) phosphate-acetate buffer of pH 6, and (3) 0.01 *M* KOH.

TABLE 1[a]

Concentration of 2-Hexylpyridine = 8.74×10^{-5} *M* OD in 10^{-2} *M* HCl = $d_I = 0.710$ cm^{-1} at 263.5 nm; OD in 10^{-2} *M* KOH = $d_M = 0.305$ cm^{-1}

pH of the buffer	d (cm^{-1})	$d - d_M$ (cm^{-1})	$d_I - d$ (cm^{-1})	$\log \frac{d - d_K}{d_I - d}$	pK
5.46	0.611	0.308	0.099	+0.493	5.95
5.60	0.602	0.299	0.108	+0.442	6.04
5.74	0.554	0.251	0.156	+0.207	5.95
5.86	0.533	0.230	0.177	+0.114	5.97
6.04	0.490	0.187	0.220	−0.70	5.97
6.07	0.496	0.193	0.214	−0.045	6.02
6.25	0.449	0.146	0.261	−0.253	6.00
6.33	0.432	0.129	0.278	−0.333	6.00
6.48	0.414	0.111	0.296	−0.427	6.05
6.65	0.381	0.078	0.329	0.625	6.02

[a] Average $pK_a^T = 6.00 \pm 0.05$. Activity correction for ionic strength of 2×10^{-2} *M* (buffer):

$$
\begin{aligned}
pK_a^T &= pK_a^M - \frac{0.505\sqrt{2 \times 10^{-2}}}{1 + 1.6\sqrt{2 \times 10^{-2}}} \\
&= pK_a^M - 0.06 \\
&= 5.94 \pm 0.05
\end{aligned}
$$

Extraction Studies of Gold

Figure 3 presents data for the extraction of gold initially at $<10^{-7}$ *M* by a 0.1 *M* solution of HPy in benzene from different mineral acid solutions. The maximum in the case of the hydrochloric acid system occurs at comparatively much lower acidity than in the corresponding nitric and sulfuric acid systems. In the case of hydrochloric acid, it is probably the high complexing ability of auric ions with chloride which causes a large fraction of the metal to be in an extractable form at a 0.1 to 0.5 *M* concentration of the supporting acid. The maxima in the case of nitric and sulfuric acid solutions occur at 1 and 2 *M*, respectively. The extraction behavior in chloride media closely parallels that of iron, indium, and gallium (*16*). In the extraction of these metals from aqueous hydrogen chloride solutions, there is also an initial steep rise with increasing acid concentration. The halogen ion concentration, at the point where the extractability rises steeply, depends on the complexity constants of the metals. The extraction isotherms in the present case are also generally similar to the corresponding NPy systems (*4*). For the sake of comparison, the extraction data of gold by NPy are reproduced in Fig. 4 from Ref. 4.

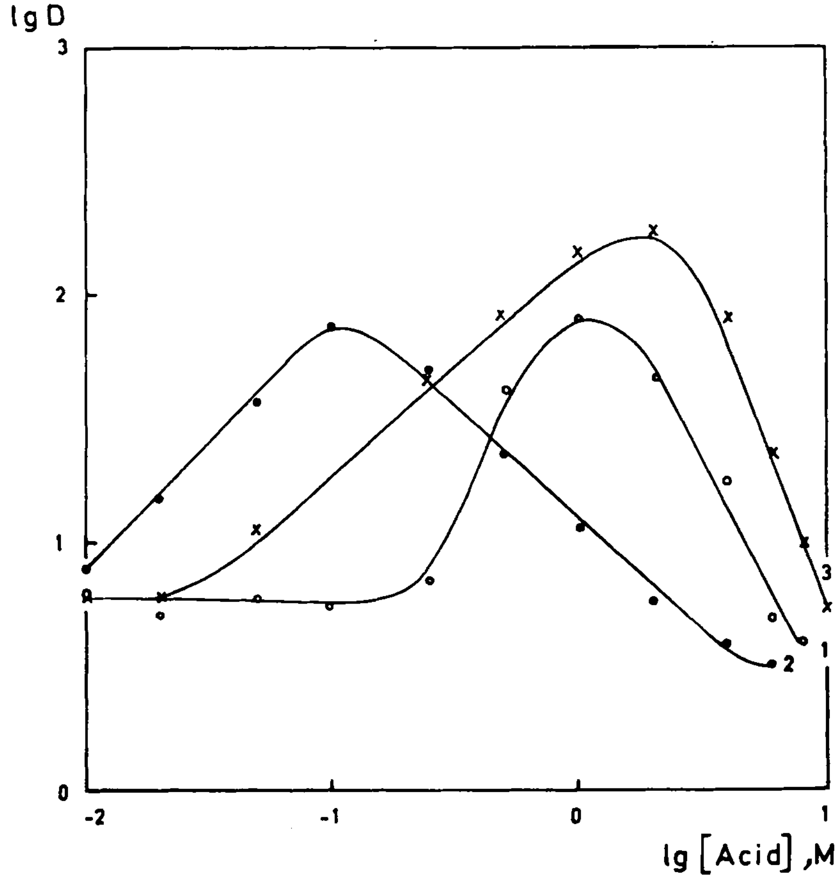

FIG. 3. D_{Au} plotted as a function of equilibrium acid concentration, C_{acid} in mole/l, organic phase = 0.1 *M* HPy/benzene: (1) HNO_3, (2) HCl, (3) H_2SO_4.

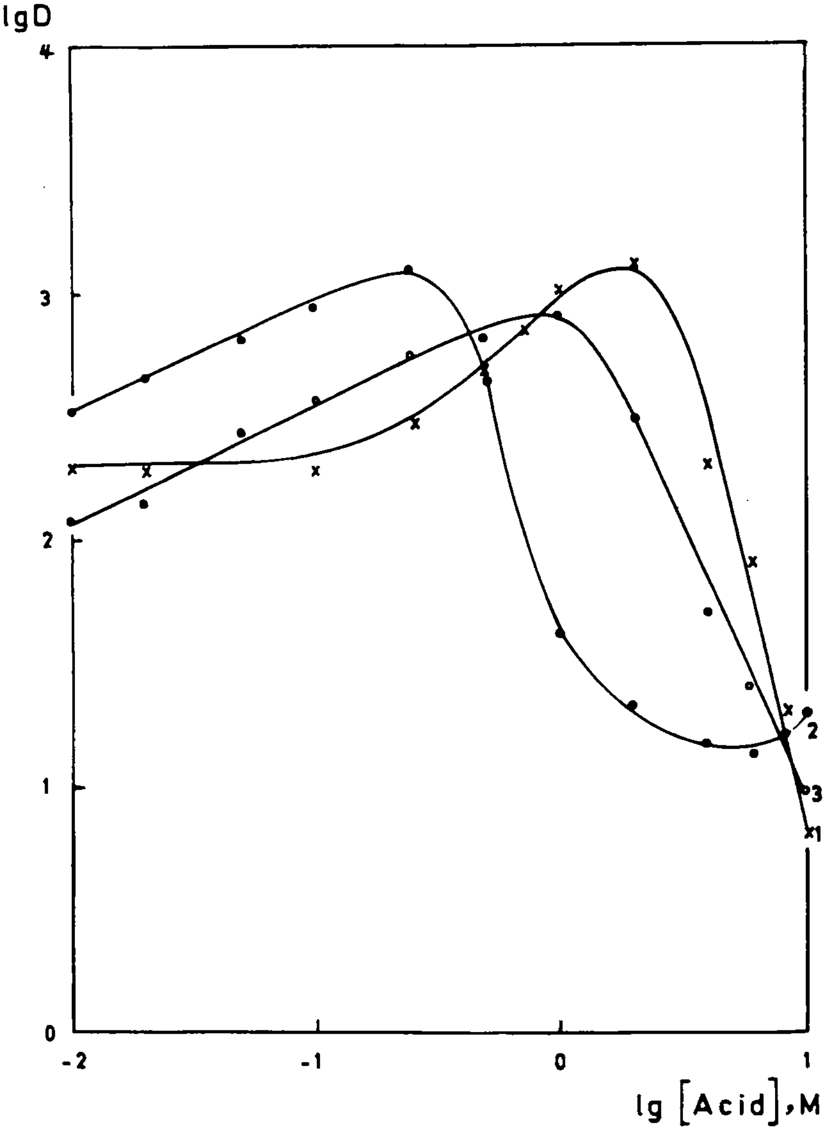

FIG. 4. D_{Au} plotted as a function of equilibrium acid concentration, C_{acid} in mole/l, organic phase = 0.1 *M* NPy/benzene: (1) HNO_3, (2) HCl, (3) H_2SO_4.

It is seen that the D values for HPy are approximately an order of magnitude lower than for NPy. This might be associated with the reduced amount of stearic hindrance in the more symmetrical NPy and the greater density at the nitrogen atom. The extracted complexes of gold are probably $AuCl_4^-$, $Au(NO_3)_4^-$, and $Au(SO_4)_2^-$, either salted out as protonated anions by the supporting acids or through the association of anionic complexes with the amine cations. The simplest generalized equation for the extraction of gold complexes can be written as

$$Au_{aq}^{3+} + 3X_{aq}^- + n(HPy.\,HX)_{org} \rightleftarrows [(HPyH)_n AuX_{3+n}]_{org} \tag{1}$$

where the subscript aq denotes the aqueous phase and org denotes the organic phase. The corresponding mass law expression, in terms of concentrations rather than activities, is

$$K = [(HPy.\,H)_n AuX_{3+n}]_{org}/[Au^{3+}]_{aq}[X^-]_{aq}^3[HPy.\,HX]_{org}^n \tag{2}$$

Among the simplifying assumptions made are that the amine salts exist as monomeric species, that a single extracted species of complex is formed, and that the activity coefficients of the various species are essentially unchanged. The D value can be written as

$$D = \frac{[(HPy.\,H)_n AuX_{3+n}]_{org}}{[Au^{3+}]_{aq}} \tag{3}$$

According to Eq. (3), at a constant concentration of chloride or nitrate ions, n can be determined from a plot of log D vs log [HPy. HX]. A test of the dependency of the extraction of Au(III) on the concentration of HPy.HX was made by varying the pyridine concentration at constant total chloride and nitrate ion concentrations. The results are summarized in Fig. 5. The linear parts of the curves show that n is 2. Presumably doubly charged complexes are extracted and/or the singly charged gold complex of the types $AuCl_4^-$, $Au(NO_3)_4^-$, and $Au(SO_4)_2^-$ are extracted by either of the following mechanisms:

$$2HPy + HX \rightleftarrows (HPy \ldots H \ldots PyH)^+X^-$$

$$(HPy \ldots H \ldots PyH)^+X^- + AuX_4^- \rightleftarrows (HPy \ldots H \ldots PyH)^+AuX_4^-$$

or through the formation of mixed quadrupoles formed by the association of the free amine salts of the mineral acids with the gold species to give

$$(HPyH^+)X^-.(HPyH^+)AuX_4^-$$

either as a dipole-dipole head to tail association of $(HPyH)^+X^-$ with

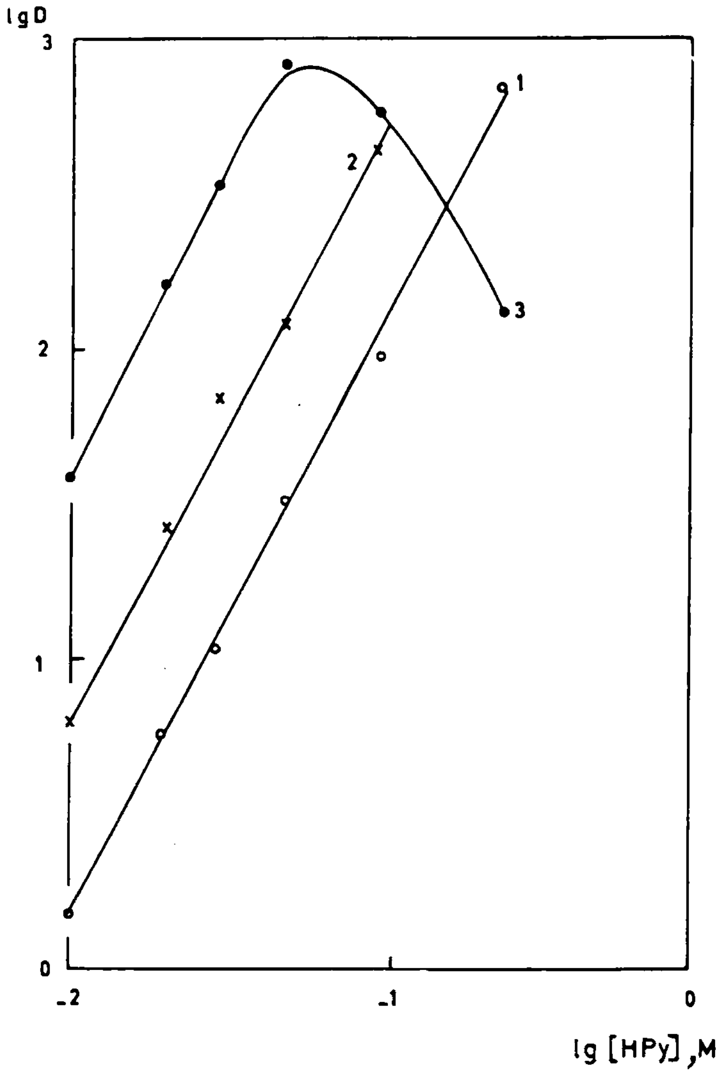

FIG. 5. Influence of the concentration of 2-hexylpyridine/benzene on the extraction coefficient of gold: (1) 1 *M* HNO_3, (2) 0.1 *M* HCl, (3) 1 *M* H_2SO_4.

$HPyH^+.AuX_4^-$ or as having two $HPyH^+$ cations hydrogen bonded to one chloride or nitrate anion. The dependence of *D* on the reagent concentration is not regular above a 0.05 *M* concentration of the amine in the case of the sulfuric acid system (Fig. 5) and in the hydrochloric acid system (Fig. 6) when the concentration of the supporting acid is 2 *M* and the slope of curve beyond 0.04 *M* concentration of the amine decreases to a negative value which is very close to 1. This, of course, can be connected with the aggregation of the pyridine salts and the association of $AuCl_4^-$

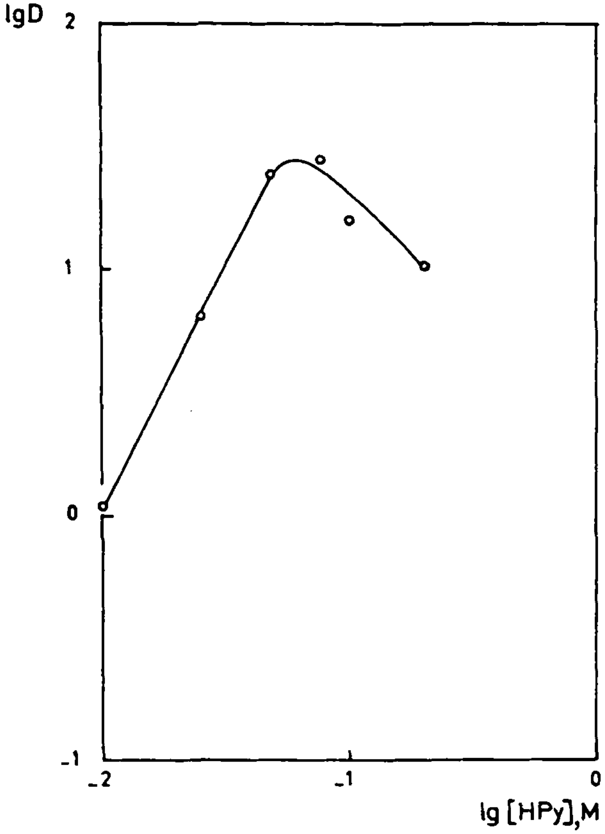

FIG. 6. Influence of the concentration of 2-hexylpyridine on the extraction coefficient of gold from 2 *M* HCl.

with monoionized aggregates:

$$\mathrm{HPyH^+ + Cl^- \rightleftarrows HPyH^+Cl^- \rightleftarrows (HPyH^+Cl^-)_2 \rightleftarrows}$$

$$\mathrm{(HPyH^+Cl^-)_n \rightleftarrows (HPyH^+Cl^-)_q}$$

$$\mathrm{(HPyH^+Cl^-)_q \rightleftarrows [(HPyH^+Cl^-)_{q-1}HPyH]^+ \ldots Cl^-}$$

This anions is then capable of reacting with the metal complex, resulting in an ion-paired complex

$$\mathrm{[(HPyH^+Cl^-)_{q-1}HPyH]^+AuCl_4^-}$$

However, when the aqueous hydrochloric acid concentration is 0.2 *M*, there is no deviation from linearity. As long as the organic phase does not contain excess acid in equilibrium [in the present case excess acid is taken up by the reagent when the initial aqueous acid concentration exceeds 2.5 *M* (*8*)]. The mass action law applied to the equilibrium of the equation

$$\mathrm{HPy_{org} + HX_{aq} = HPyHX_{org}}$$

can also give information on the form in which the salt exists in the organic phase by plotting the log-log plot of

$$\mathrm{[HPyHX]_{org}/[HPy]_{org}} \text{ versus } a_{\mathrm{HX}}$$

where $\mathrm{[HPy]_{org}}$ represents the total concentration of the free pyridine. The value of slope *n* can enable one to distinguish between:

(a) the existence of nondissociated ion pairs ($n = 1$):

$$\mathrm{[HPyHX]_{org} = [HPyH^+ \ldots X^-]_{org}}$$

(b) their dissociation ($n < 1$):

$$\mathrm{[HPyHX]_{org} = [HPyH^+ \ldots X^-]_{org} + [HPyH^+]_{org}}$$

(c) their association ($n > 1$):

$$\mathrm{[HPyHX]_{org}} = \sum n\mathrm{[(HPyH^+ \ldots X^-)_n]_{org}}$$

The plot of $\mathrm{[HPyHX]_{org}/[HPy]_{org}}$ versus HCl concentrations (instead of activities) gave a slope of approximately 1 (Fig. 7) below 1 *M* HCl, indicating that a 0.1 *M* benzene solution of the amine exists in the form of a monomeric species when the acid concentration is less than 1 *M*. This indicates that the increase in concentration of HCl also increases polymerization. Similar results were encountered in the case of NPy extraction of Cr(VI)

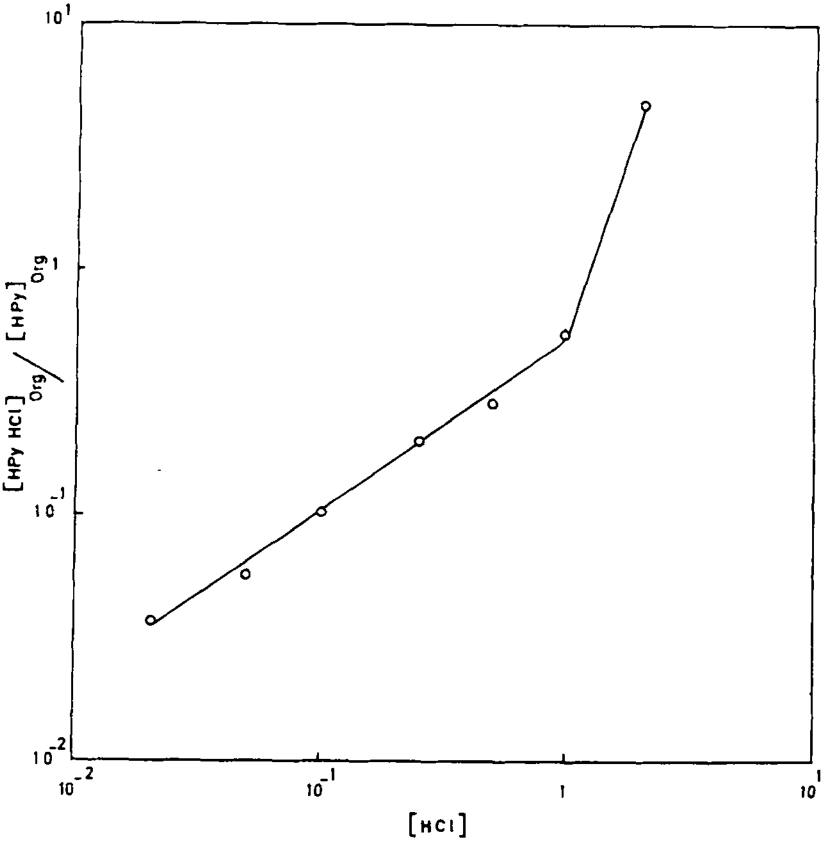

FIG. 7. Log-log plot of $[HPyHCl]_{org}/[HPy]_{organic(free)}$ vs [HCl].

from hydrochloric acid solutions (*3*). This shows that amine hydrochloride aggregates depolymerize with decreasing hydrochloric acid concentration in the initial aqueous phase, or probably when free amine base is present in the system. The phenomenon may well be explained by a specific solvation of the amine salt by the amine base. Such an organic phase can be regarded as a solution of the amine salt in a binary solvent mixture of the amine base and the diluent. The selective solvation is a dipole-dipole interaction, where the amine base molecule, with its low but permanent dipole, has a greater tendency than the diluent to accumulate in the vicinity of the large dipole of the amine salt. Such a shielding of the polarity of the pyridine ion-pair probably stabilizes it and prevents its aggregation, similar to the aliphatic amine systems (*17*, *18*). In these experiments it was found that the linearity of the plot of logarithm of extraction coefficient against the logarithm of the pyridine concentration broke down at very low concentrations of the pyridine when trace concentrations of the metal are employed, probably because the diluent itself contributed slightly toward the extraction process.

An interpretation of the distribution data for the sulfuric acid system in terms of mass-law action is apparently more difficult than for hydrochloric and nitric acids due to the equilibria in amine sulfate and amine bisulfate formation, polymerization of sulfate- and bisulfate-bearing species, the equilibria in the sulfate–bisulfate exchange in the aggregates, and the partition equilibria of various sulfate–bisulfate aggregates.

The effect of common anions on the extraction of gold was investigated and the results are presented in Fig. 8. The addition of neutral chloride ions (sodium chloride) to the constant acidity solutions of hydrochloric

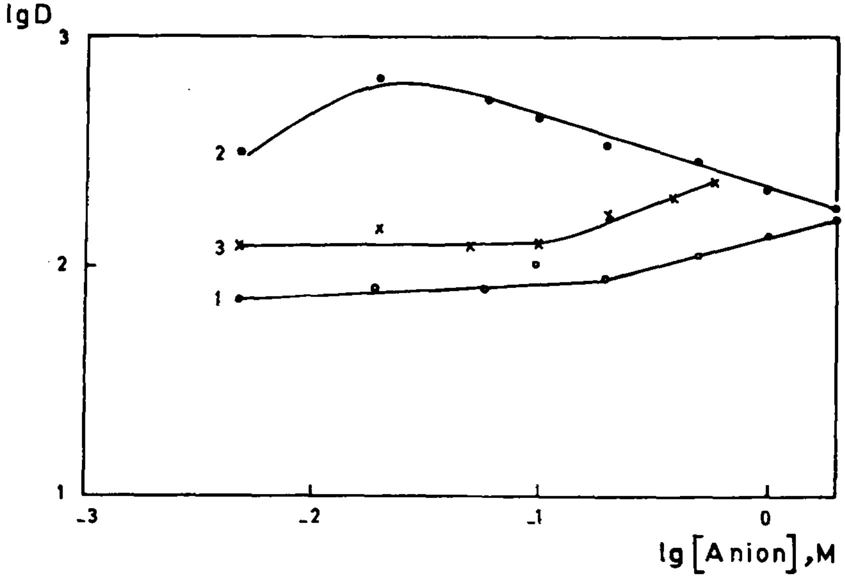

FIG. 8. Influence of initial concentrations of salt on distribution ratios of Au, organic phase = 0.1 *M* HPy/benzene: (1) $NaNO_3$ (1 *M* HNO_3), (2) NaCl (0.1 *M* HCl), (3) Na_2SO_4 (2 *M* H_2SO_4).

acid (0.1 *M*) corresponding to the extraction maximum appears to have a salt-out effect up to about 0.05 *M* concentration of added chloride ions. A further increase in the salt concentration leads to a decrease in the extraction, possibly due to the formation of less extractable chloride complexes. In the case of nitrate and sulfate ions added to the corresponding constant acidity solutions, an increase in extraction is observed when the concentration of the added salts increases above 0.1 *M*. This shows that common anions do not have a depressing effect on the extraction.

The extraction of gold was also studied as a function of the concentration of different anions added to the constant acidity solutions of hydrochloric, nitric, and sulfuric acids corresponding to the extraction maxima. In the chloride system (Fig. 9) the addition of acetate ions to 0.1 *M* hydrochloric acid first shows a slight increase in the distribution coefficient up to 0.05 *M* concentration. A further increase in the concentration of added acetate ions (as sodium acetate) leads to a sharp decrease in the extraction coefficient of gold, probably due to a shift in the equilibrium species favoring the formation of unextractable complexes. The effect of citrate ions closely resembles that of acetate ions but the decrease in extraction is less pronounced. In the case of oxalate, there is a steady decrease in the distribution coefficient up to 0.25 *M* concentration of the added salt and a sharp decrease with increasing concentration. Thiocyanate ions show a steady decrease, but in the case of ascorbic acid the extraction isotherm shows an anomolous increase in the *D* values up to 0.25 *M* concentration. The effects of the addition of various neutral anions to 1 *M* nitric acid are seen in Fig. 10. Acetate, citrate, and oxalate ions decrease the distribution coefficient only at concentrations greater than 0.05 *M*. In the case of thiocyanate the *D* value decreases up to 0.05 *M*, after which it starts leveling off. The extraction isotherm in the case of ascorbic acid has a maximum at 0.5 *M*.

In the sulfuric acid system (Fig. 11) the addition of acetate ions has little effect on the extraction which remains more or less constant. The addition of citrate ions results in a steady decrease of the distribution coefficient after 0.01 *M* concentration, and loss of activity was observed at concentrations greater than 0.5 *M*. Oxalate and thiocyanate ions decrease the *D* values while ascorbic acid gives an extraction maximum at 0.1 *M*, which is similar to the corresponding nitric and hydrochloric acid systems.

Gold extracted in the organic phase from the mineral acid solution can easily be back-extracted by 4% ammonia solution or by adding 0.05 *M* sodium thiosulfate solution in 0.1 *M* HCl or in 1 *M* HNO_3. The stripping action of thiosulfate ion in these acids is not clearly understood.

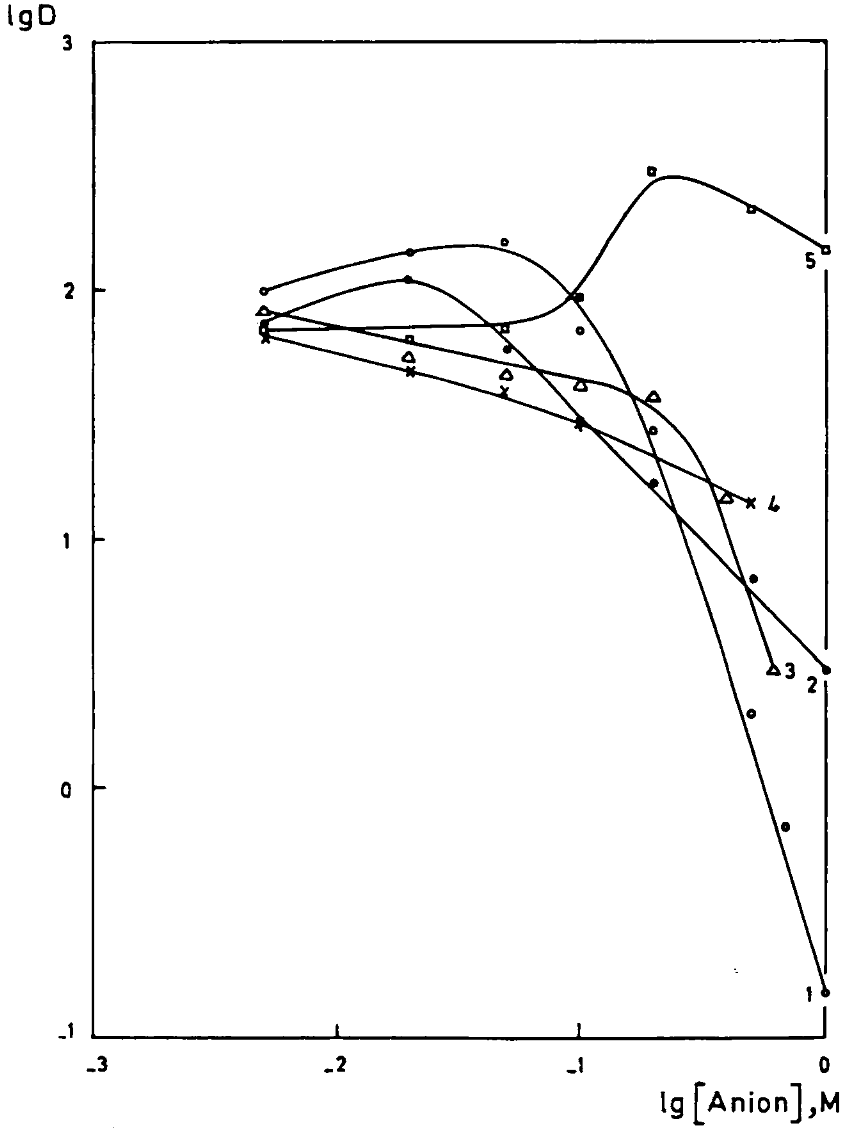

FIG. 9. Effect of various anions on the extraction of gold from 0.1 *M* hydrochloric acid by 0.1 *M* HPy/benzene: (1) acetate, (2) citrate, (3) oxalate, (4) thiocyanate, (5) ascorbic acid.

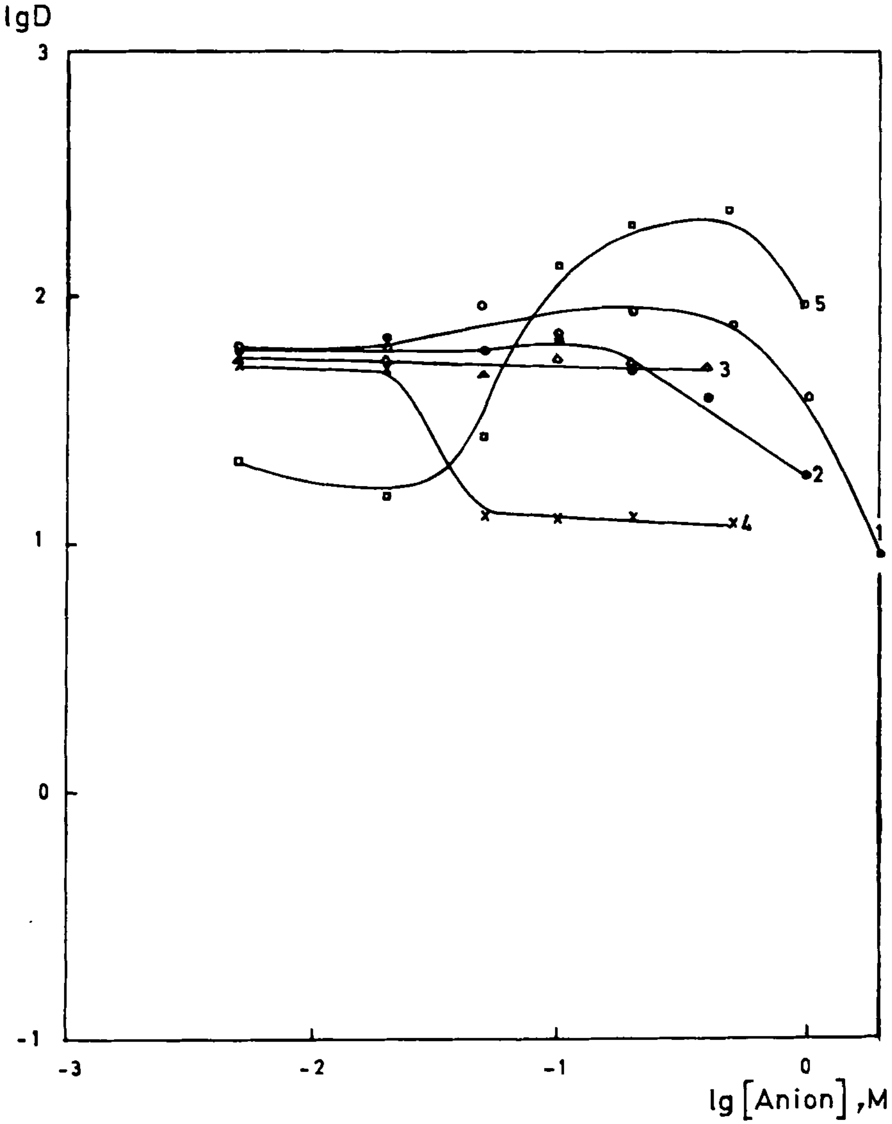

FIG. 10. Effect of various anions on the extraction of gold from 1 *M* nitric acid by 0.1 *M* HPy/benzene: (1) acetate, (2) citrate, (3) oxalate, (4) thiocyanate, (5) ascorbic acid.

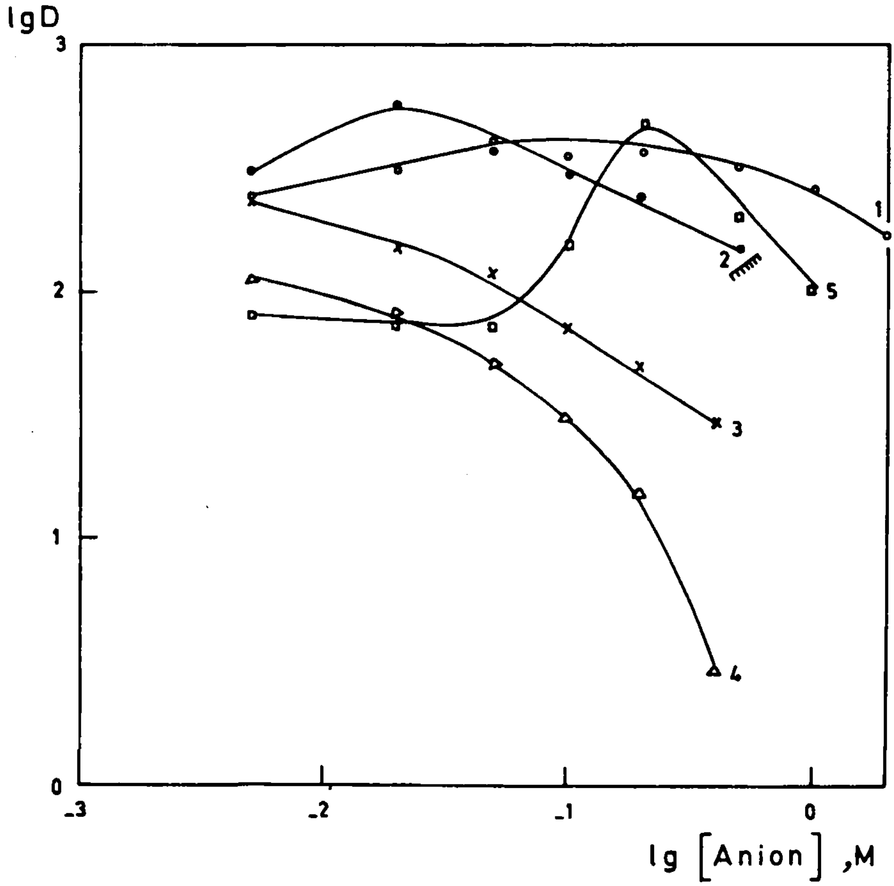

FIG. 11. Effect of various anions on the extraction of gold from 2 *M* sulfuric acid by 0.1 *M* HPy/benzene: (1) acetate, (2) citrate, (3) oxalate, (4) thiocyanate, (5) ascorbic acid.

The selectivity of the extraction separation of gold with 0.1 *M* HPy in benzene was studied with 0.1 *M* hydrochloric acid. The behavior of a number of metal ions including uranium, thorium, iron, and important fission products was examined. Figure 3 suggests that the optimal hydrochloric acid concentration is 0.1 to 0.5 *M*. The data presented in Table 2 show that the extraction of gold is very selective. The separation factor, S.F., is defined as the ratio of the extraction coefficients of two elements

TABLE 2

Separation Factors of Different Metal Ions Relative to Gold in 0.1 *M* HPy/Benzene–Mineral Acid Extraction Systems

Metal	Concentration (mole/l)[a]	Separation factors D_{Au}/D_M		
		0.1 *M* HCl	1 *M* HNO_3	2 *M* H_2SO_4
U(VI)	10^{-3}	10^5	—	10^5
Cr(VI)	10^{-6}	2×10^4	3×10^4	10^5
Th(IV)	C.F.	10^7	—	—
Fe(III)	10^{-7}	10^5	10^6	10^6
Y(III)	C.F.	10^7	10^6	10^7
La(III)	C.F.	10^7	10^6	10^7
Ce(III)	10^{-8}	10^7	10^6	10^7
Pm(III)	10^{-8}	10^7	10^6	10^7
Tb(III)	10^{-8}	10^7	10^6	10^7
Ba(II)	10^{-8}	10^6	10^5	10^4
Sr(III)	10^{-9}	10^6	10^5	10^4
Ca(III)	10^{-8}	10^6	10^7	10^5
Mn(II)	10^{-8}	10^6	10^6	10^5
Ni(II)	10^{-7}	10^6	10^7	10^6
Co(II)	10^{-8}	10^6	10^6	10^6
Mg(II)	10^{-5}	10^5	10^5	10^6
Cu(II)	10^{-5}	10^5	10^5	10^6
Zn(II)	10^{-8}	—	10^7	—
Cs	10^{-8}	10^6	10^6	10^6
Na	10^{-6}	10^6	10^7	10^6

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

extracted under identical conditions. Iron, which generally contaminates the extraction of gold by phosphorous- and carbon-bonded oxygen-donor extractants and high molecular weight amines, is not extracted along with gold from 0.1 to 3 *M* HCl concentration. The only interfering element is Cr(VI) whose separation factor at trace concentrations of the metal is fairly good but decreases considerably where macroamounts of the metal are present. Cr(VI) can be masked by adding sodium citrate to the sample solution [0.5 *M* sodium citrate is enough to hold back up to 0.05 *M* Cr(VI)] while the extraction of gold remains quantitative.

Procedure for the Separation and Estimation of Gold by Neutron Activation Analysis

Various types of samples were spiked with known amounts of gold and irradiated for 1 hr at 1.5×10^{13} $nsec^{-1}cm^{-2}$. The irradiated material was

TABLE 3

Analysis of Samples by the Proposed Method. Sample Composition

Matrix[a]	Gold (μg) Taken	Gold (μg) Found	% Error
Na (50), K (50), Ca (50), Mg (50)	50	50.20	+0.40
Ni (50), Co (50), Mn (50), Cr (50)	100	100.7	+0.80
Ca (50), Mg (50), Zn (50), Ce (50)	50	49.6	−0.80
Ca (50), Mg (50), Al (50), Fe (50), Y (50), Ce (50), Na (50)	100	99.6	−0.40
Co (50), Ni (50), Mn (50), Cr (50), Zn (50), La (50), Sr (50)	100	97.3	−2.70
Ba (50), Sr (50), Cs (50), Na (50), K (50), Ca (50), Ni (50), Co (50)	50	50.3	+0.60

[a] Number in parentheses are milligrams of element.

treated with aqua regia, filtered, and heated to dryness. The residue was dissolved in 0.1 *M* hydrochloric acid and shaken with an equal volume of 0.1 *M* HPy benzene for 5 min. The organic phase was scrubbed twice with 0.1 *M* HCl. The radiochemical purity of the extract was checked by γ-spectra and decay studies. An aliquot of the extract was counted at a suitable geometry for ^{198}Au by integrating the area under the 0.411-MeV peak. All activity measurements were made 4 hr after the end of the irradiation. The standards were treated identically. The amount (W) of gold in the sample (Table 3) was calculated by

$$W = \frac{WsA}{As}$$

where Ws is the weight of the standard and A and As are the activities of the samples prepared and the standard, respectively.

The results of various samples of different matrix composition are presented in Table 3.

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