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 Ejaz, M. , Qureshi, Mudassar A. and Zuha, Shamas Ud(1981) 'Radiochemical Studies on the Extraction of Trace Amounts of Mercury(II) from Aqueous Iodide Solutions Using 4-(5-Nonyl) Pyridine as a Solvent', Separation Science and Technology, 16: 3, 291 — 302

To link to this Article: DOI: 10.1080/01496398108068520

URL: http://dx.doi.org/10.1080/01496398108068520

SEPARATION SCIENCE AND TECHNOLOGY, 16(3), pp. 291–302, 1981

Radiochemical Studies on the Extraction of Trace Amounts of Mercury(II) from Aqueous Iodide Solutions Using 4-(5-Nonyl) Pyridine as a Solvent

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Abstract

Results are reported for the liquid-liquid extraction of trace amounts ($\sim 10^{-8}$ *M*) of mercury(II) from aqueous iodide solutions by 4-(5-nonyl) pyridine (NPy) in benzene. The data indicate that mercury(II) can be extracted with extremely high partition values from water and a wide range of hydrochloric, nitric, and sulfuric acid concentrations with only 0.01–0.1 *M* NPy. 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, iodide ions, salting and complexing agents, and the solvent concentration. Common salts have little effect on extraction in concentrations up to 1 *M*. Regeneration of the solvent is achieved by stripping mercury with moderately concentrated nitric acid. The effects of various complexing agents on the extraction of the metal are described. Distribution coefficients and separation factors of several metal ions relative to mercury(II) are also reported for the optimal concentrations of the mineral acid solutions containing 0.2 *M* potassium iodide. Ferric iron does not interfere with extraction. The investigation reveals that 4-(5-nonyl) pyridine is a better extractant for iodide complexes of mercury than the commonly used primary, secondary, tertiary, and quaternary amines.

INTRODUCTION

Solutions of high-molecular-weight pyridine amines act as liquid anion exchangers, the exchange properties of which are similar to those of organic ion-exchange resins (*1*, *2*), and also as solvating reagents under certain experimental conditions (*3*). In a recent paper (*4*) we described a new system for the extraction of zinc with 4-(5-nonyl) pyridine from aqueous iodide solutions, and showed that under certain experimental conditions this pyridine, because of its low basicity (*2*), behaves as a better extractant than the commonly used aliphatic amines and carbon- and phosphorous-bonded oxygen donor solvents. This communication presents recent fundamental work on the extraction of mercury(II) from aqueous solutions of hydrochloric, nitric, and sulfuric acids containing iodide ions which, because of their low aqueous hydration, give stable complexes with mercury that are very efficiently extracted by this pyridine from water and mineral acid solutions through solvation. Furthermore, it has the advantage that mercury can be quantitatively extracted in a single extraction from alkaline, neutral, and acidic solutions over some fairly wide range of acidities so that there would be some allowable error in adjusting the acid concentration of the solution.

EXPERIMENTAL

Reagents and Procedure

4-(5-Nonyl) pyridine (NPy) was used as an extractant. The characteristics of this compound are given elsewhere (*4*, *5*). Laboratory double-distilled water was used. ^{203}Hg tracer solutions were prepared by dissolving a known amount of irradiated HgO in high purity acids and diluting to volume with distilled water. The distribution ratios were measured by equilibrating 1 mL of the aqueous phase containing approximately 10^6 gamma counts/100 s/mL of ^{203}Hg tracer at room temperature (24 ± 3°C) with equal volumes of 0.1 *M* NPy/benzene (except for the solvent effect) in 20 mL glass vials. In slope analyses the organic phases had been presaturated with the barren aqueous phases by repeated contacting. A 3-min mixing period was selected although equilibrium was attained more rapidly. After equilibration, the vials were centrifuged and aliquot parts from each phase were analyzed for mercury-203 by counting in a gamma scintillation counter. The equipment used for the radiochemical assay is described elsewhere (*1*, *6*).

RESULTS AND DISCUSSION

In the first series of experiments the extraction of mercury(II) by 0.1 *M* NPy/benzene from hydrochloric, nitric, and sulfuric acid solutions was studied. The results are shown in Fig. 1(A). In the hydrochloric acid system the extraction in dilute and moderate acid solutions may be due to the extraction of neutral and/or anionic chloride complexes of mercury(II) which exist in this range of acidity. The decrease in extraction with increasing aqueous acidity can be attributed to the competition of the acid for the base or due to the formation of less extractable metal complexes. In nitric and sulfuric acid solutions the extraction from weakly acid solutions can be attributed to the extraction of neutral species of the metal. The decrease in extraction at high acidities can be explained similarly to the chloride system. In sulfuric acid media, loss of activity was observed above 1 *M* concentration. This may be due to the formation of an invisible third phase caused due to the lower solubility of $(NPyH)^+HSO_4^-$ in benzene, as the amine hydrogen sulfates are generally less soluble than the corresponding sulfates (*7*), perhaps because the former are more aggregated.

The extraction of mercury(II) was also studied from aqueous iodide solutions (0.02 and 0.1 *M*) with varying concentrations (0.01–10 *M*) of the mineral acids whereby the organic phase was 0.1 *M* NPy/benzene. The results presented in Figs. 1(B) and 1(C) show that under these conditions mercury(II) is quantitatively extracted over a wide range of acid concentrations and $\log D$ vs $\log[\text{acids}]$ curves shift markedly toward higher D values. This is probably because HgI_2 is more organophilic than $HgSO_4$, $HgCI_2$, or $Hg(NO_3)_2$. In all the three mineral acid systems, the extraction isotherms show maxima at around 0.5 *M* acid concentrations. In the hydrochloric and sulfuric acid systems the partition value decreases when the concentration of these acids in the initial aqueous solutions exceeds 0.5 *M*, but the extraction still remains quantitative even up to 10 *M* concentration of the supporting acids. In the sulfuric acid system, turbidity appears in the aqueous phase beyond 0.5 *M* concentration. In nitric acid media there is a sharp decrease of partition value as the concentration of nitric acid in the original aqueous solutions exceeds 0.5 *M* and is perhaps due to the competitive coextraction of the molecular nitric acid by the pyridine. The organic phase became dark red above 4 *M* HNO_3, possibly due to the coextraction of molecular iodine liberated by the oxidation of potassium iodide.

The results of the extraction experiments in which the distribution ratios were measured as a function of the iodide concentration are presented in Fig. 2. The iodide dependence of the partition value shows the same general trend in most cases. There is a general rise in distribution coefficient with increase of iodide concentration, a maximum at about 0.2 *M* iodide and a slight decrease in the partition to the highest concentration measured. It is to be noted from Fig. 2 that very high extraction coefficients are obtained from very dilute acid solutions in the presence of 0.1–1 *M*

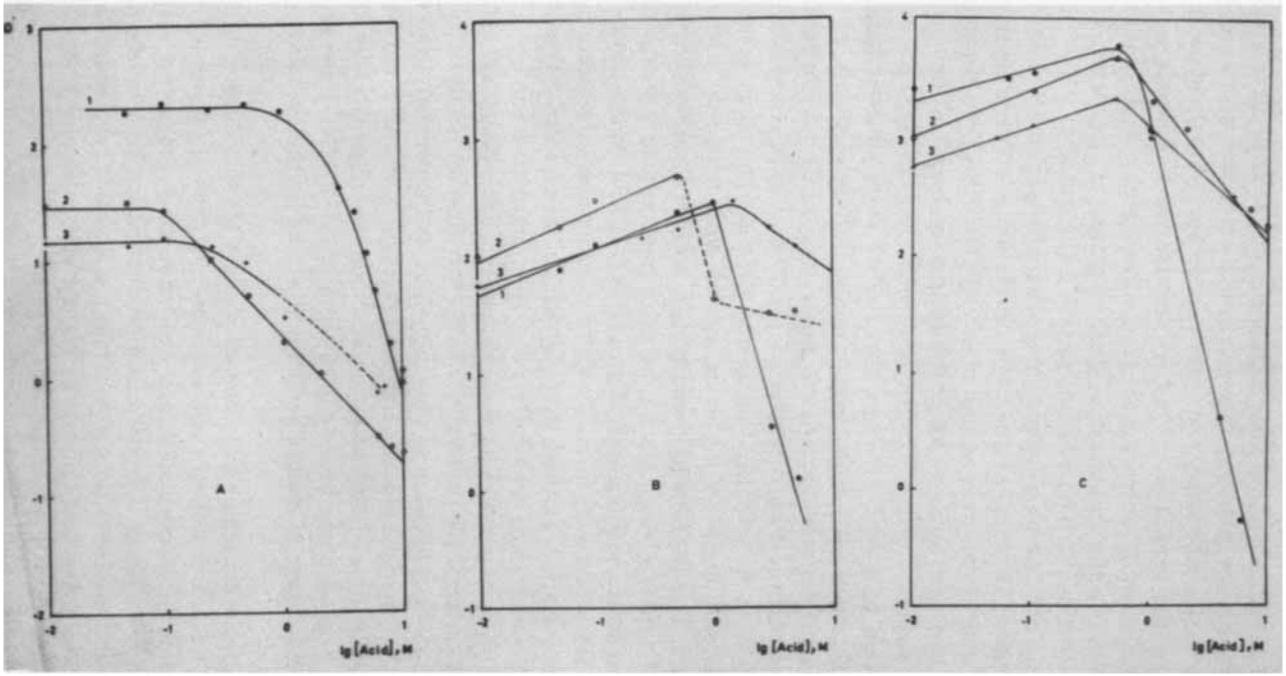

FIG. 1. (A) Distribution coefficient of Hg(II) between aqueous mineral acid solutions and 0.1 *M* NPy/benzene: (1) HCl, (2) HNO_3, (3) H_2SO_4. (B) Distribution coefficient of Hg(II) between aqueous mineral acid solutions containing 0.02 *M* potassium iodide and 0.1 *M* NPy/benzene: (1) HCl, (2) HNO_3, (3) H_2SO_4. (C) Distribution coefficient of Hg(II) between aqueous mineral acid solutions containing 0.1 *M* potassium iodide and 0.1 *M* NPy/benzene: (1) HCl, (2) HNO_3, (3) H_2SO_4.

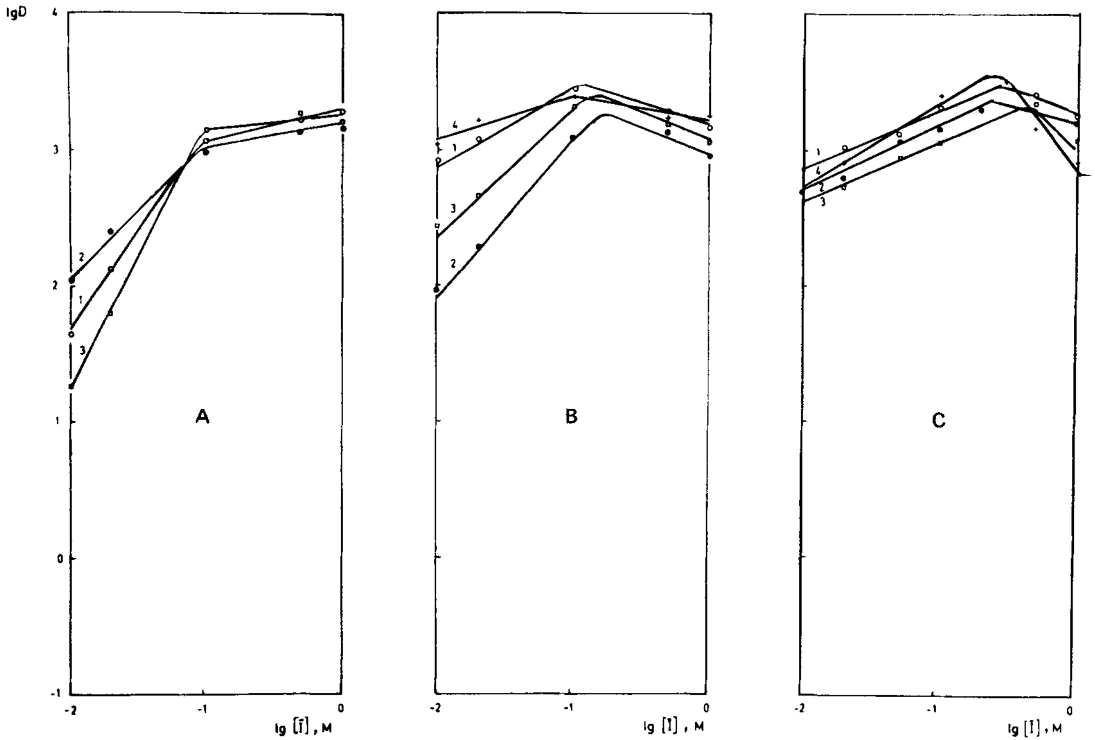

Fig. 2. Variation of the partition coefficient of Hg(II) with iodide concentration from constant acidity solutions by 0.1 *M* NPy/benzene. (A) C_{HCl}: (1) 0.01 *M*, (2) 0.2 *M*, (3) 1.0 *M*. (B) C_{HNO_3}: (1) 0.01 *M*, (2) 0.1 *M*, (3) 0.5 *M*, (4) 1.0 *M*. (C) $C_{H_2SO_4}$: (1) 0.01 *M*, (2) 0.1 *M*, (3) 0.5 *M*, (4) 1.0 *M*.

potassium iodide. Furthermore, the experiments in our laboratory have shown that mercury(II) is also extracted quantitatively with partition coefficient values greater than 5×10^2 from neutral and alkaline aqueous iodide solutions (0.02–1 *M*) by 0.1 *M* NPy/benzene. A comparison of our data with those of primary, secondary, and tertiary amines (*8*) shows that the present extractant is superior to the aliphalic amines for the extraction of mercury(II) from aqueous potassium iodide solutions. The present reagent is even superior to quaternary amines (*8*) which extract mercury fairly efficiently from dilute acid solution because only about 0.2% solution of this pyridine is sufficient for quantitative extraction while the quaternary amine requires at least 10 times more (2%) concentrated solution for achieving completeness of extraction. In addition, unlike the quaternary amine, mercury(II) can easily be back-extracted from the organic phase with moderately concentrated nitric acid solution. No degradation of the reagent occurs, obviously because resonance makes the molecule very stable.

Experiments were performed to ascertain the composition of the extractable species by extracting mercury(II) at fixed concentrations of the mineral acids with varying concentrations of NPy using benzene as a diluent. When the partition coefficients are plotted on a log-scale against the pyridine concentrations, also on a log-scale (Fig. 3), straight lines are not obtained. Instead, curves are obtained which can be resolved into three straight sections, indicating the extraction of different complexes.

The effect of common salts on the extraction of mercury(II) was investigated from the corresponding constant acidity solutions containing 0.2 *M* potassium iodide. The results are shown in Fig. 4. The addition of neutral sodium chloride to the constant acidity solutions of hydrochloric acid does not greatly influence the partition values of mercury up to 1 *M* concentration of the added neutral salt. This is probably because the addition of sodium chloride results in the formation of chloride complexes of the metal which are also quantitatively extracted. The extraction increases above 1 *M* concentration of the salt, evidently due to the salting-out effect. In the case of sodium nitrate and sulfate (Fig. 4), the extraction decreases slightly at relatively high salt concentrations, probably because the nitrate and sulfate complexes of mercury formed at high concentration of the corresponding salts are less extractable and the effects of the shift of equilibrium of species and that of salting-out act in opposite directions, resulting in an overall decrease of partition value.

The effect of various complexing agents on the extraction of mercury(II), under the optimal conditions, from the mineral acid solutions containing potassium iodide (0.2 *M*) was investigated. The results are shown in Fig. 5. Citrate, oxalate, and acetate decrease the partition coefficient values,

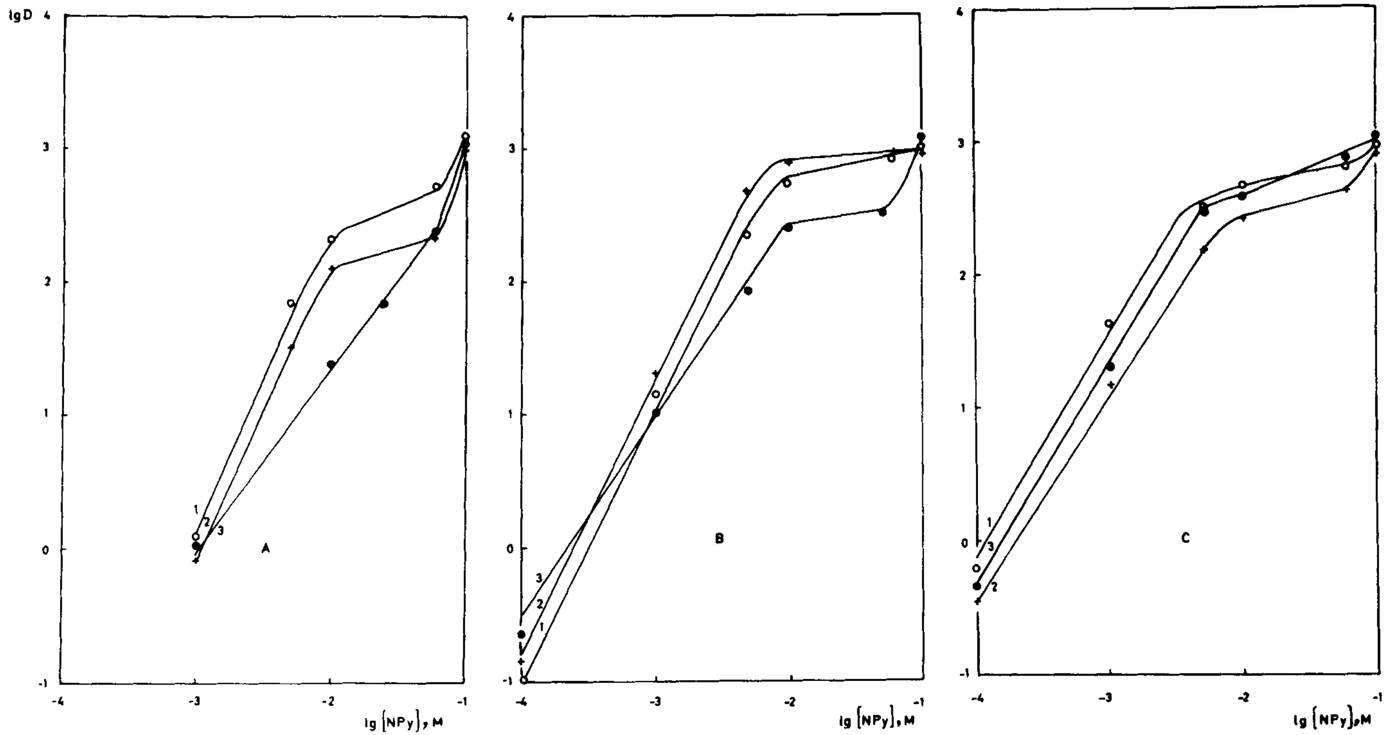

Fig. 3. Variation of the partition coefficient of Hg(II) with the pyridine concentration in benzene. (A): (1) 0.1 *M* HCl, (2) 0.1 *M* HNO_3, (3) 0.1 *M* H_2SO_4. (B): (1) 0.5 *M* HCl, (2) 0.5 *M* HNO_3, (3) 0.5 *M* H_2SO_4. (C): (1) 1.0 *M* HCl, (2) 1.0 *M* HNO_3, (3) 1.0 *M* H_2SO_4.

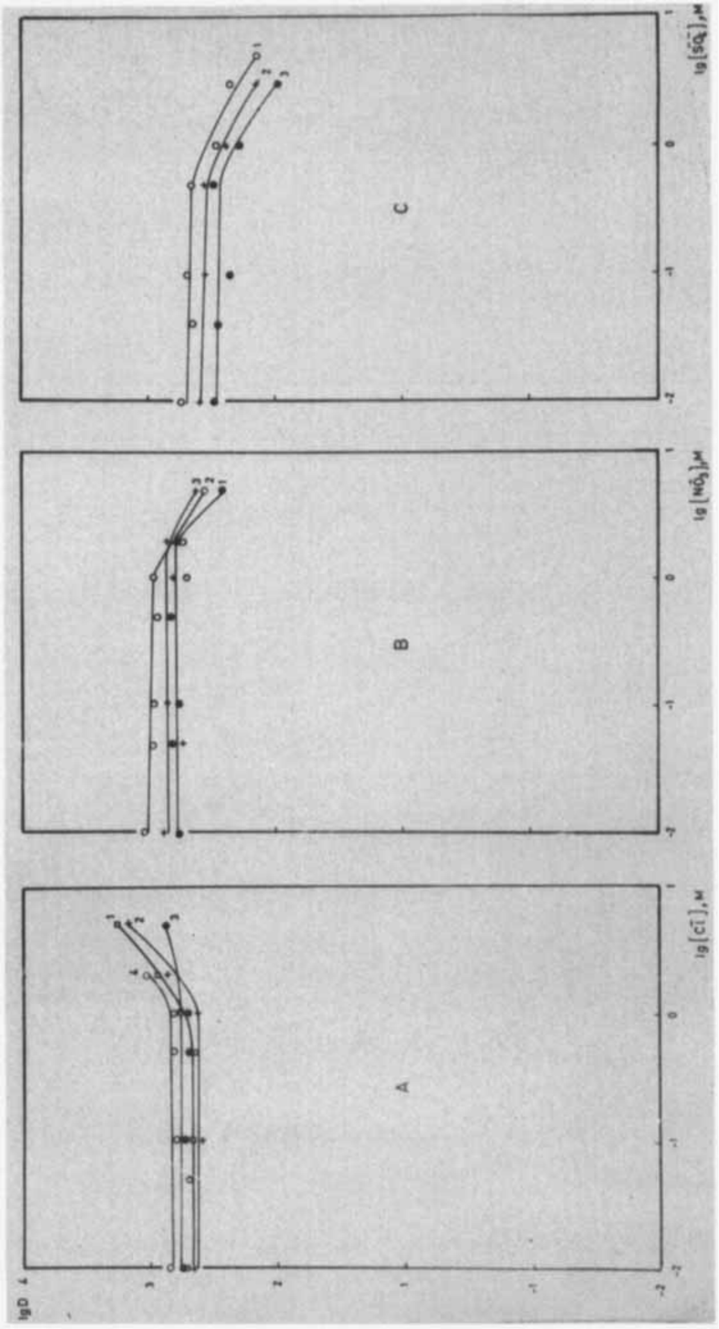

FIG. 4. Effect of the addition of neutral chloride, nitrate, and sulfate ions on the partition coefficient of Hg(II) from constant acidity solutions which were 0.2 *M* with respect to iodide ion by 0.1 *M* NPy/benzene. (A) C_{HCl}: (1) 0.01 *M*, (2) 0.1 *M*, (3) 1.0 *M*, (4) 2.0 *M*. (B) C_{HNO_3}: (1) 0.01 *M*, (2) 0.1 *M*, (3) 1.0 *M*. (C) $C_{H_2SO_4}$: (1) 0.01 *M*, (2) 0.1 *M*, (3) 1.0 *M*.

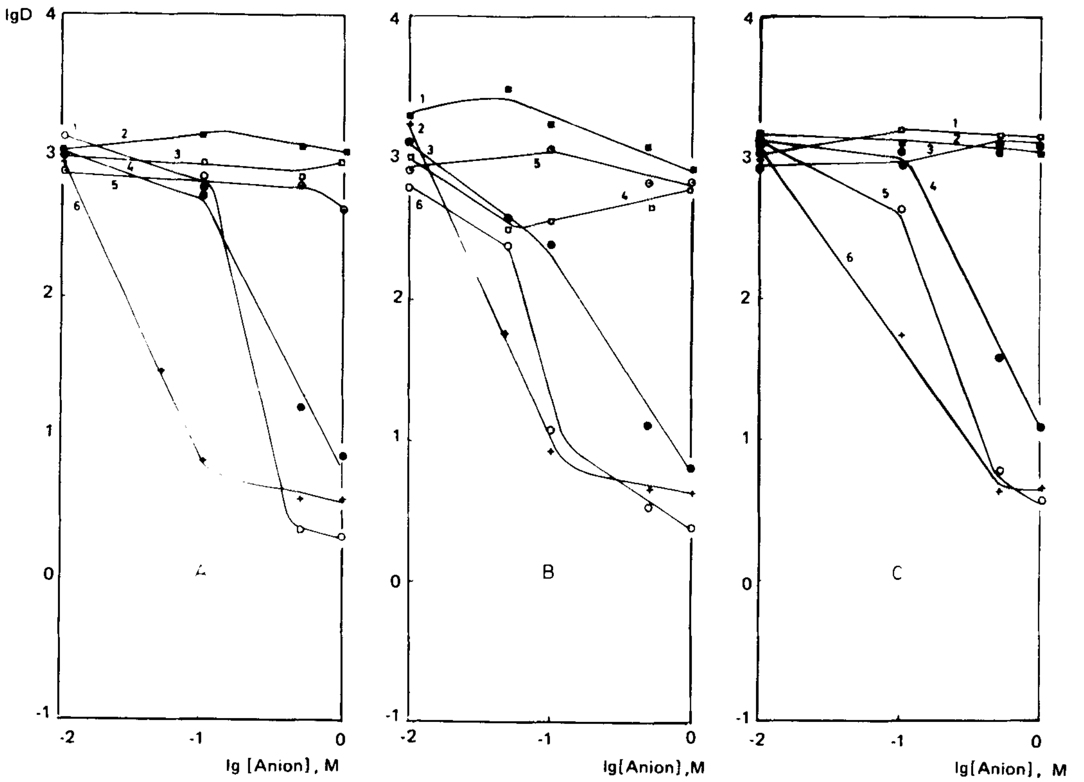

FIG. 5. Effect of the addition of various anions on the partition of Hg(II) with 0.1 *M* NPy/benzene from constant acidity solution containing 0.2 *M* KI. (A) $C_{HCl} = 0.1$ *M*: (1) acetate, (2) ascorbate, (3) nitrate, (4) oxalate, (5) sulfate, (6) citrate. (B) $C_{HNO_3} = 0.1$ *M*: (1) ascorbate, (2) citrate, (3) oxalate, (4) chloride, (5) sulfate, (6) acetate. (C) $C_{H_2SO_4} = 0.1$ *M*: (1) chloride, (2) ascorbate, (3) nitrate, (4) oxalate, (5) acetate, (6) citrate.

but the decrease is not strongly pronounced. In the case of other anions, the partition value remains more or less constant. These results indicate that none of these complexing agents can be employed for the back-extraction of mercury(II). However, concentrated nitric and perchloric acids, presumably due to their low aqueous hydration, strip mercury quantitatively from the organic phase.

The selectivity of the extraction separation of mercury(II) was studied from 0.1 *M* solutions of hydrochloric, nitric, and sulfuric acids containing 0.2 *M* potassium iodide. The distribution coefficients and separation factors of a number of metal ions are reported in Table 1. It is seen that the extraction of mercury is very selective and the separation factors of most of the test elements, including Fe(III), are greater than 10^3. These separation factors can be improved further by carrying out the extraction of mercury(II) with only a 10^{-2} *M* solution of NPy instead of 10^{-1} *M* because under these conditions the extraction of mercury is still quantitative (Fig. 1B) while the extraction of other elements, e.g., zinc, decreases with a slope of 2. The results indicate that mercury(II) can be very selectively separated from a large number of elements in a single extraction followed by 2 or 3 scrub stages which will barely affect the recovery of the metal (because of high *D* values) while eliminating the impurities from the organic extract. Thus for removal of mercuric ions as a preconcentration step, the reagent offers the most promise because of selectivity, completeness of extraction, and short equilibration period. Furthermore, the metal can be extracted from water and a fairly wide range of acidities much more efficiently than the commonly used liquid–anion-exchangers, and close control of acidity is unnecessary. In addition, aqueous to organic ratios up to 100 to 1 can be utilized without loss of extraction efficiency, and data can be efficiently used in water pollution studies requiring the addition of only a single complexing agent which is normally desired to reduce the adsorption of the trace metal. No adjustment of the pH prior to chemical separation or preconcentration is required, which thus reduces the adjustment steps which are generally a source of contamination even when efforts are made to use high purity reagents.

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Note Added in Proof. Correspondence and requests for reprints should be sent to M. Ejaz.

Received by editor August 15, 1980