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Mutual Influence of Iron(III) and Gold(III) as Macroconstituents in the Extraction Systems Forming Three Liquid Phases*

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Abstract

The extraction of a mixture of iron(III) and gold(III) by either pure or diluted (benzene as diluent) diisopropyl ether (IPE) from aqueous solutions of hydrochloric acid at 20°C was investigated. The dependence of metal extraction on the initial concentration of hydrochloric acid, iron(III), and IPE was studied under conditions of third phase formation. It was found that under certain conditions, gold(III) coextracted with iron(III).

INTRODUCTION

It is well known that the phenomenon of mutual influence of constituents must be taken into consideration as a possible drawback during the application of solvent extraction processes. There are much data in the literature about the influence of macroelements on microelements as well as about the mutual influence of microelements, but there are only a few data about the mutual influence of macroelements. In the systems including a solvent of relatively low dielectric constant, such as diisopropyl ether (IPE), coextraction most frequently appears, while solvents with a relatively high dielectric constant cause suppression of the extraction.

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Coextraction is explained by the formation of mixed ion associations in the organic phase which contain both extracted elements. Due to their importance in the development of new separation procedures, it was interesting to study three-phase systems and the mutual influence of elements in such a more complex partition.

The system $FeCl_3$–$AuCl_3$–HCl–H_2O–IPE–C_6H_6 was used as a model. Benzene performs the function of an inert diluent. Previous investigations of the extraction of either iron(III) or gold(III) by pure and diluted IPE from hydrochloric acid solution showed a striking difference in the behavior of the above-mentioned metals (*1–3*).

EXPERIMENTAL

Materials

IPE was purified with saturated iron(II) chloride solution followed by treatment with sodium hydroxide solution. After washing with water it was distilled and the middle fraction (bp 66.8–67.8°C at 744 mmHg) collected. IPE prepared in this way contained 1.95 mg H_2O/mL.

Gold(III) chloride solutions were prepared using metallic gold (refined, 99.9%) or gold(III) chloride tetrahydrate (48% min).

Other chemicals used were of analytical reagent grade.

Apparatus

The separations were made in 25 and 50 mL separation funnels having a calibrated stem and/or in 15 mL graduated cuvettes which were selected from a large group in order to assure accurate volume calibrations.

Measurements of UV absorption were made on a Hilger Uvispek Spectrophotometer.

Procedure

Investigation was made by conventional technique. The systems were prepared by vigorous shaking of predetermined components and placed in a water bath with a thermostat held by automatic control at 20.0 ± 0.05°C. The shaking was repeated in the same manner at 15-min intervals for 1 h.

The initial volume ratio of the organic phase to the aqueous phase (r^i) was always 1.0. The volumes of the equilibrate phases were determined before sampling. Sampling for analysis by pipettes thermostated at the temperature of extraction was carried out directly (from the cuvette) or after removal of the separated phases (from the funnel).

The systems were prepared with various initial concentrations of metals or acid in the initial aqueous phase or with various initial concentrations of IPE in the initial organic phase. All the data obtained are the results of two or more repeated experiments, dependent on the degree of reproducibility.

Methods of Analysis

The concentration of metals in the samples of aqueous phase and in the pretreated samples of organic phases was determined by UV spectrophotometry, complexometric titration (for larger quantities of iron), or gravimetry (for larger quantities of gold).

Absorbance of iron(III) and gold(III) was measured at 335 and 226 nm, respectively, and at a fixed hydrochloric acid concentration. Complexometric titration was carried out using Titriplex III and 2-oxy-5-sulfobenzoic acid as the indicator. Gravimetric analysis using zinc as the reducing agent was applied without previous treatment of the organic phase samples.

RESULTS AND DISCUSSION

The results obtained show the influence of iron(III) on the gold(III) content in equilibrate phases. It was also found that the volume of the heavy organic phase in the extraction of both metals together was larger than the sum of the heavy organic phase volumes obtained in the extraction of the single elements under the same conditions.

Under the investigated conditions (extraction by pure IPE, initial concentrations of components: $c_{\mathrm{Au}}{}^{i} = 0.069\ M$ and $c_{\mathrm{HCl}}{}^{i} = 8.9\ M$) the increase in the initial concentration of iron(III), in a range from 0.074 to 0.220 *M*, causes a decrease of gold(III) concentration in the heavy and light organic phases (Fig. 1) but an increase of the distribution ratio of gold(III) ($D_c{}^{\mathrm{Au}}$). Corresponding distribution ratios, extraction factors, and separation factors are shown in Table 1. At the same time the distribution ratio of iron(III) ($D_c{}^{\mathrm{Fe}}$) passes through the maximum value and the separation factor gold(III)/iron(III) ($\alpha_{\mathrm{Fe}}{}^{\mathrm{Au}}$) through the minimum value. Distribution ratio (total) in the systems with three liquid phases is generally given by

$$D_c = (D_c)_{\mathrm{aq}}{}^{h} + (D_c)_{\mathrm{aq}}{}^{l} \tag{1}$$

or

$$D_c = (D_c)_{\mathrm{aq}}{}^{h}[1 + 1/(D_c)_l{}^{h}] \tag{2}$$

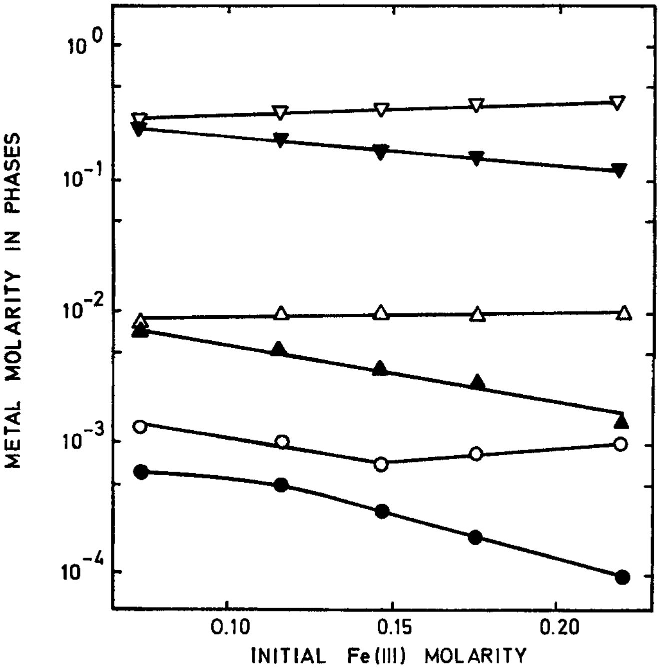

FIG. 1. Metal concentration in the equilibrate phases vs the initial iron(III) concentration. System: $AuCl_3$–$FeCl_3$–HCl–H_2O–IPE. Initial concentration of components: $c_{Au}{}^i = 0.069\ M$ and $c_{HCl}{}^i = 8.9\ M$. Initial phase volume ratio $r^i = 1.0$. Aqueous phase data: (○) for iron(III) and (●) for gold(III). Light organic phase data: (△) for iron(III) and (▲) for gold(III). Heavy organic phase data: (▽) for iron(III) and (▼) for gold(III).

where $(D_c)_{aq}{}^h$ is the partial distribution ratio between the heavy organic phase and the aqueous phase, $(D_c)_{aq}{}^l$ is the partial distribution ratio between the light organic phase and the aqueous phase, and $(D_c)_l{}^h$ is the partial distribution ratio between the heavy organic phase and the light organic phase (*1*). The partial distribution ratio $(D_c)_{aq}{}^h$ mostly contributes to a value of the distribution ratio in the extraction systems containing IPE. In the above-mentioned case (Table 1), the partial distribution ratio of iron(III) $(D_c{}^{Fe})_l{}^h$ changes only slightly but the partial distribution ratio of gold(III) $(D_c{}^{Au})_l{}^h$ increases. Due to the increase of the heavy organic phase volume (Table 2), the partial extraction factor between the heavy organic phase and the aqueous phase $(D_m{}^{Au})_{aq}{}^h$ is especially increased (Table 1).

The influence of the initial IPE concentration was investigated at 11 *M* initial acid concentration ($c_{Au}{}^i = 0.069\ M$ and $c_{Fe}{}^i = 0.074\ M$). Metal concentration in the organic phases was independent (in the three-phase region) of the initial IPE concentration (Fig. 2), but the concentration of

TABLE 1

Distribution Ratios, Separation Factors, and Extraction Factors of Iron(III) and Gold(III) at Various Initial Concentrations of Iron(III)[a]

Initial iron(III) molarity	D_c^{Au}	D_c^{Fe}	α_{Fe}^{Au}	$(D_c^{Au})_l^h$	$(D_c^{Fe})_l^h$	$(D_c^{Au})_{aq}^h$	$(D_m^{Au})_{aq}^h$
0.074	366	191	1.9	38	35	337	77
0.117	402	306	1.3	38	31	342	104
0.147	542	507	1.1	44	39	530	179
0.176	735	420	1.7	48	38	720	284
0.220	1215	363	3.3	80	39	1200	581

[a] System: $AuCl_3$–$FeCl_3$–HCl–H_2O–IPE. Initial concentrations of components: $c_{Au}^i = 0.069$ *M* and $c_{HCl}^i = 8.9$ *M*. Initial phase volume ratio $r^i = 1.0$. Temperature 20°C. D_c^{Au} and D_c^{Fe} are the distribution ratios of gold(III) and iron(III), respectively; α_{Fe}^{Au} is the separation factor gold(III)/iron(III); $(D_c^{Au})_l^h$ and $(D_c^{Fe})_l^h$ are the partial distribution ratios between the heavy organic phase and light organic phase of gold (III) and iron(III), respectively; $(D_c^{Au})_{aq}^h$ is the partial distribution ratio between the heavy organic phase and the aqueous phase of gold(III); and $(D_m^{Au})_{aq}^h$ is the partial extraction factor between the heavy organic phase and the aqueous phase of gold(III).

TABLE 2

Volumes of Coexisting Phases at Various Initial Concentrations of Iron(III)[a]

Initial iron(III) molarity	Volume (mL)		
	Aqueous phase	Heavy organic phase	Light organic phase
0.074	7.0	1.5	3.2
0.117	6.8	1.8	3.1
0.147	6.8	2.3	2.7
0.176	6.6	2.6	2.4
0.220	6.4	3.1	2.2

[a] System: $AuCl_3$–$FeCl_3$–HCl–H_2O–IPE. Initial concentrations of components: $c_{Au}^i = 0.069$ *M* and $c_{HCl}^i = 8.9$ *M*. Initial phase volume ratio $r^i = 1.0$. Temperature 20°C.

metals in the aqueous phase increases rapidly due to an increase in the initial IPE concentration and causes a decrease in the corresponding distribution ratios.

The influence of initial hydrochloric acid concentration was investigated with pure (7.1 *M*) and diluted IPE (4.7 *M*). In the case of pure IPE (in the range of 7 to 9 *M* initial hydrochloric acid concentration) the concentration of metals increases in the heavy organic phase while it decreases in the light organic phase (Fig. 3). This results in an increase of the partial distribution

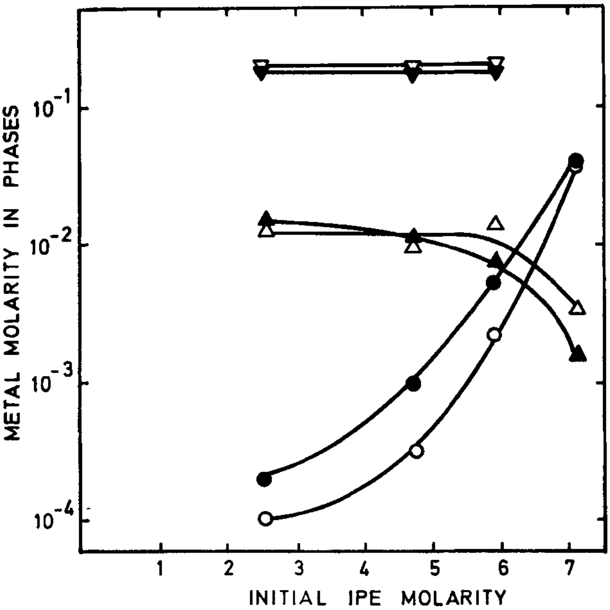

FIG. 2. Metal concentration in the equilibrate phases vs the IPE concentration in the organic solvent. System: $AuCl_3$–$FeCl_3$–HCl–H_2O–IPE–C_6H_6. Initial concentration of components: $c_{Au}{}^{i} = 0.069\ M$, $c_{Fe}{}^{i} = 0.074\ M$, and $c_{HCl}{}^{i} = 11.0\ M$. Initial phase volume ratio $r^{i} = 1.0$. Aqueous phase data: (○) for iron(III) and (●) for gold(III). Light organic phase data: (△) for iron(III) and (▲) for gold(III). Heavy organic phase data: (▽) for iron(III) and (▼) for gold (III).

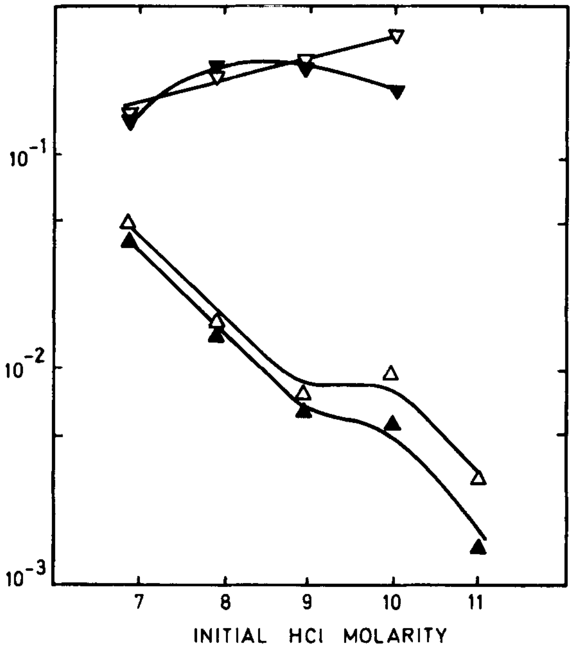

FIG. 3. Metal concentration in the equilibrate phases vs the initial hydrochloric acid concentration. System: $AuCl_3$–$FeCl_3$–HCl–H_2O–IPE. Initial concentration of components: $c_{Au}{}^i = 0.069$ *M* and $c_{Fe}{}^i = 0.074$ *M*. Initial phase volume ratio $r^i = 1.0$. Light organic phase data: (△) for iron(III) and (▲) for gold(III). Heavy organic phase data: (▽) for iron(III) and (▼) for gold(III).

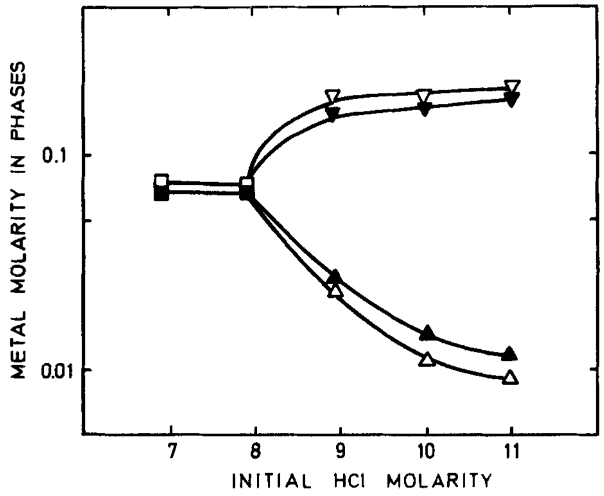

FIG. 4. Metal concentration in the equilibrate phases vs the initial hydrochloric acid concentration. System: $AuCl_3$-$FeCl_3$-HCl-H_2O-IPE-C_6H_6. Initial concentration of components: $c_{Au}{}^i = 0.069$ *M*, $c_{Fe}{}^i = 0.074$ *M*, and $c_{IPE}{}^i = 4.7$ *M*. Initial phase volume ratio $r^i = 1.0$. Organic phase data: (□) for iron(III) and (■) for gold(III). Light organic phase data: (△) for iron(III) and (▲) for gold(III). Heavy organic phase data: (▽) for iron(III) and (▼) for gold(III).

TABLE 3

Molar Ratios of Metals at Different Conditions of Extraction[a]

Initial molar ratio Fe/Au	1.07	1.71	2.14	2.55	3.19
Equilibrate molar ratio Fe/Au in the heavy organic phase	1.07	1.66	2.18	2.62	3.25

[a] Initial concentrations of components: $c_{Au}{}^i = 0.069$ *M*, $c_{HCl}{}^i = 6.9$–11.0 *M*, and $c_{IPE}{}^i = 2.5$–7.1 *M*. Initial phase volume ratio $r^i = 1.0$. Temperature 20°C.

ratio between the heavy organic phase and the light organic phase. When diluted IPE was used, the similarity of the curves describing the changes of metal concentration in the organic phases was very definite (Fig. 4). In the three-phase region the concentrations of gold(III) and iron(III) were practically the same in both of the phases in the whole region investigated. There is also strong agreement between the initial metal molar ratio and the metal molar ratio in the equilibrate organic phase (Table 3). Such behavior confirms a mechanism of mixed ion association formation, probably of type $H^+FeCl_4{}^-H^+AuCl_4{}^-$, similar to the ion associations proposed in the case of the coextraction of indium(III) in the presence of iron(III) (*4*).

One can conclude that gold(III) is coextracted in the presence of iron(III) when both of them are in macro amounts, and that the coextraction is independent of the initial molar ratio of the metals in the range investigated.

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