# Radiotracer Study of Synergistic Effects of Neutral Donors on the Extraction of Gold with *N*-(Thioacetyl)benzamide in Chloroform<sup>1</sup>

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**Abstract**—The extraction of Au(III) from an aqueous acidic medium with *N*-(thioacetyl)benzamide in chloroform was studied in the presence of organophosphorus donors (tributylphosphine oxide, triphenylphosphine oxide, tributyl phosphate) at pH 3.0 using radiotracer technique. The influence of various parameters on the extraction equilibrium was examined. The extent of extraction of Au(III) in the form of the binary complex increases with temperature, but the reverse trend is observed with the ternary complex. The overall equilibrium constants for each of the three ternary extraction systems were estimated, and the role of different thermodynamic functions is discussed. The extraction mechanism is supported by the IR spectra of the ternary adduct.

Keywords: synergistic extraction, N-(thioacetyl)benzamide, gold-198

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The phenomenon of synergism, when two extractants used in combination extract a metal ion much more efficiently as compared to the normal additive effect of these extractants used separately, has been extensively studied from both theoretical and practical points of view. Various combinations of extractants causing synergistic effects in metal ion extraction have been described [1–7]. An additional extractant seems to play an important role, presumably replacing the coordinated water molecules to form organophilic adducts with the metal–ligand complexes.

The liquid–liquid extraction of Au(III) from aqueous acidic medium has long been studied [8–10]. Being a soft cation, it tends to form complexes with soft bases like thiourea and substituted thioureas, which was used [11–15] for the gold transfer into a nonpolar organic medium. Amides and their derivatives are promising extractants for many metal ions. Numerous studies describe the extraction with amides [16–18]. This study deals with the extraction of Au(III) spiked with <sup>198</sup>Au radiotracer into chloroform with a newly synthesized complexing agent, *N*-(thioacetyl)benzamide, and with the effect of various phosphine oxides and tributyl phosphate on such extraction. The organophosphorus compounds used in this study are wellknown neutral donors capable of dehydrating the metal ions, facilitating their transfer into an organic medium [19, 20]. However their effect on the Au(III) extraction is less studied [21, 22], and such a study might be of paramount importance in the field of hydrometallurgy. The effects of various parameters (concentration of ligand and organophosphorus donors, temperature, etc.) are reported. The role of mixed extractants has been elucidated in terms of such effects.

## EXPERIMENTAL

Chemicals and devices. The chelating extractant, N-(thioacetyl)benzamide, was synthesized by the reaction of benzoic acid and thioacetamide, which were obtained from Aldrich, USA. The donor reagents used in this study (tributyl phosphate, TBP; tributylphosphine oxide, TBPO; triphenylphosphine oxide TPPO) were also purchased from Aldrich. The solvents were purified by standard procedures. All the other chemicals used were of A.R. grade. A stock solution of gold was prepared by dissolving AuCl<sub>3</sub> (Johnson Matthey) in deionized water and standardized by gravimetry [23]. A working solution (~230 ppm) was prepared by appropriate dilution. An appropriate volume of the stock solution of Au(III) was mixed with a few drops of a tracer solution containing <sup>198</sup>Au as AuCl<sub>3</sub>, supplied by BRIT (India), and finally

<sup>&</sup>lt;sup>1</sup> The text was submitted by the authors in English.



**Scheme 1.** Synthesis of the chelating ligand, *N*-(thioace-tyl)benzamide.

brought to the mark. The CHN microanalysis of the synthesized ligand was made with a Perkin–Elmer 2400 CHNS-O elemental analyzer. The IR spectra of the ligand and adducts were recorded with a Perkin–Elmer FTIR Model RX1 spectrometer. A Systronics model 335 digital pH-meter equipped with a single electrode was used for pH measurement. A single-channel  $\gamma$ -ray spectrometer coupled with a well-type NaI(Tl) detector (Nucleonix, India) was used for radio-activity measurements. The <sup>198</sup>Au tracer was assayed by its 412 keV photopeak.

**Extraction.** In the general extraction procedure, 5 ml of an aqueous solution containing  $\sim 100 \ \mu g$  of spiked Au(III) was adjusted to pH 3.00 and extracted with an equal volume of chloroform solution of the chelating extractant for 30 min in a mechanical shaker. For synergistic study, the organic phase was mixed with appropriate donor reagent of desired concentration. After the equilibration, the two phases were separated and the radioactivities of equal volumes of both phases were measured. The distribution ratios *D* were calculated as the radioactivity ratio of the organic and

**Table 1.** Effect of diluents on the extraction of Au(III) from aqueous chloride medium

Diluent	$D_0$	<i>E</i> , %
Chloroform	20.21	95.28
Methyl isobutyl ketone	19.14	95.04
Isoamyl alcohol	15.24	92.64
<i>n</i> -Butanol	10.45	91.26
Toluene	5.42	84.42
Carbon tetrachloride	4.26	80.98
Xylene	2.11	67.84
Benzene	1.41	58.51

aqueous phases, with checking the material balance.

Synthesis and characterization of the chelating agent. The chelating ligand was synthesized by the general condensation reaction between benzoyl chloride and thioacetamide (1 : 1). The starting material, A.R. grade benzoic acid (2.00 g), was refluxed for 2 h with successive addition of thionyl chloride. Excess chlorinating agent was removed by slow evaporation. In a beaker, a saturated solution of thioacetamide (1.24 g) in double-distilled anhydrous nitrobenzene was prepared. The solvent was purified by drying over calcium oxide, followed by distillation before use. This thioacetamide solution was then condensed with benzoyl chloride for 1 h on a boiling water bath. The brown precipitate formed in the process was filtered off, recrystallized from chloroform, and dried. The dried compound melts at  $94 \pm 2^{\circ}$ C. The proposed formula of the ligand (Scheme 1) is in good agreement with the analytical and spectroscopic (IR, <sup>1</sup>H NMR) data. Found, %: C 60.26, H 4.98, N 7.65. Calculated, %: C 60.33, H 5.02, N 7.82. The IR spectrum of the ligand does not contain the band at  $3760 \text{ cm}^{-1}$  (v<sub>OH</sub> in the initial acid) but contains a narrow band at 1689 cm<sup>-1</sup> (carbonyl group) [24], which shows that only the hydroxy group of the acid is involved in the condensation reaction. The  $v_{C=S}$  band at 1175 cm<sup>-1</sup> confirms the preservation of the thione group of thioacetamide in the reaction. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.6 (5H, aromatic protons), 2.3 (s, 3H, methyl group), 8.1 (s, 1H, NH) [25].

#### **RESULTS AND DISCUSSION**

Effect of equilibration time. The equilibration time for the extraction of Au(III) with *N*-(thioacetyl)-benzamide in CHCl<sub>3</sub> was within 30 min. An increase in the equilibration time to 1 h did not affect the extraction equilibrium.

Effect of organic diluents. The extraction with  $1.65 \times 10^{-2}$  M extractant in benzene, toluene, xylene, methyl isobutyl ketone (MIBK), CHCl<sub>3</sub>, CCl<sub>4</sub>, isoamyl alcohol, and *n*-butanol was studied at pH 3.0. From the distribution data, CHCl<sub>3</sub> and MIBK appeared to be the most effective. The distribution ratio  $D_0$  (Table 1) increases in the order benzene < xylene < CCl<sub>4</sub> < toluene < *n*-butanol < isoamyl alcohol < MIBK < CHCl<sub>3</sub>.

Effect of pH in aqueous phase. The extraction of Au(III) from chloride solution with  $2.83 \times 10^{-2}$  M extractant in CHCl<sub>3</sub> was studied as a function of pH over the range of pH 1.0–4.0. The extraction of Au(III) was

only 6% at pH ~1.7. With an increase in pH, the extraction regularly increased and became quantitative at pH 3.0–4.0. The plot of  $\log D_0$  vs. pH (in the pH range 2.0–3.0) is a straight line with a slope of ~3 (Fig. 1), indicating that three protons were liberated on complexation of Au(III) with the extractant to give the extractable species in the organic phase.

**Extraction of Au(III) with** *N*-(thioacetyl)benzamide (HA). Extraction of Au(III) from HCl solutions was studied with CHCl<sub>3</sub> as diluent. The extractant concentration was varied from  $0.33 \times 10^{-2}$  to  $3.5 \times 10^{-2}$  M (Table 2). The extraction percentage increases with an increase in the ligand concentration. At higher concentration of the extractant, it efficiently displaces water molecules from the coordination sphere of the hydrated gold ion, which makes the complex much more organophilic. At pH 3.0, the log–log plot of  $D_0$ vs. extractant concentration is linear with a slope of ~2.89 (Fig. 2). This fact indicates that three molecules of bidentate HA ligand are involved in the extraction of gold:

$$Au_{aq}^{3+} + 3HA_{org} \rightleftharpoons [AuA_3]_{org} + 3H_{aq}^{+}.$$
 (1)

The extraction equilibrium constant k for the binary system is related to the distribution ratio by

$$\log D_0 = \log k - 3\log[\text{HA}] - 3\text{pH}.$$
 (2)

**Extraction with pure neutral donors (S).** Among the three organophosphorous compounds, tributyl phosphate (TBP) does not noticeably extract Au(III) under the examined conditions. Two phosphine oxides, TBPO and TPPO, however, noticeably extract Au(III) from aqueous solution at pH 3, with the distribution ratio ( $D_S$ ) increasing with the donor concentration. Slope analysis shows that only one molecule of any donor per AuCl<sub>3</sub> molecule is involved in the extraction.

Synergistic extraction of gold complexes in the presence of donors. The distribution ratio of Au(III) extracted with HA increases on adding organophosphorus compound S. This is attributable to the formation of a more lipophilic adduct with these donors. In the ternary extraction system, the  $\log(D_m - D_0)$  ( $D_m$  is the distribution ratio in the presence of HA and S) vs.  $\log[HA]$  plots have a slope of ~3 (Fig. 3), whereas the  $\log(D_m - D_0)$  vs.  $\log[S]$  plots are straight lines with a slope of ~1 (Fig. 4), suggesting extraction of the species AuA<sub>3</sub>·S. The overall reaction of the synergistic extraction of the gold ion is given by Eq. (3):



**Fig. 1.** Plot of  $\log D_0$  vs. pH of aqueous the phase for the extraction of Au(III) with a solution of HA in chloroform. Slope 2.79.



**Fig. 2.** log–log plot of Au(III) distribution ratio  $D_0$  in the extraction with a solution of HA in chloroform vs. extractant molar concentration. Slope 2.89.



**Fig. 3.** log–log plot of  $D_m - D_0$  vs. extractant concentration in chloroform at fixed donor concentration. Donor, concentration (mM), slope: (1) TBP, 0.38, 2.69; (2) TBPO, 0.25, 2.73; and (3) TPPO, 0.23, 2.76.

$$Au_{aq}^{3+} + 3HA_{org} + S_{org} \rightleftharpoons [AuA_3 \cdot S]_{org} + 3H_{aq}^{+}.$$
 (3)

The equilibrium constant K in the ternary system is

$$K = [AuA_3 \cdot S]_{org} [H^+]^3_{aq} / ([Au^{3+}]_{aq} [HA]^3_{org} [S]_{org}).$$
(4)

**Table 2.** Exaction of Au(III) with a solution of HA in chloroform at pH 3.0 without organophosphorus donors

Concentration, mM	$D_0$	<i>E</i> , %
3.3	0.245	19.67
6.6	0.540	35.06
9.9	5.50	84.61
16.5	20.7	95.39



**Fig. 4.** log–log plot of  $D_m - D_0$  vs. organophosphorus donor concentration in chloroform at fixed extractant concentration of 6.6 mM. Donor, slope: (1) TBPO, 0.891; (2) TPPO, 0.832; and (3) TBP, 0.826.

It is related to the distribution ratio  $D_{\rm m}$  by

 $\log K = \log (D_{\rm m} - D_0) - 3\log [{\rm HA}] - \log [{\rm S}] - 3p{\rm H}.$  (5)

It is clear from Eq. (5) that, at fixed H<sup>+</sup> and HA concentrations, the slope of the  $\log(D_m - D_0)$  vs.  $\log[S]$  dependence will correspond to the number of donor molecules in the adduct. Similarly, the slope of the  $\log(D_m - D_0)$  vs.  $\log[HA]$  at fixed H<sup>+</sup> and donor

**Table 3.** Synergistic extraction of Au(III) with a mixture of chelating extractant and organophosphorus donor. Extractant concentration 6.6 mM, pH 3.0, chloroform,  $D_0 = 0.540^{a}$ 

Donor	[Donor], mM	$D_{\rm S}$	$D_{\rm m}$	<i>E</i> , %	SC	logβ
TBPO	0.25	0.019	1.22	54.95	0.338	3.704
	0.49	0.051	1.76	63.76	0.473	3.663
	0.74	0.064	2.19	68.53	0.561	3.615
ТРРО	0.23	0.031	0.99	49.75	0.239	3.561
	0.35	0.061	1.19	54.34	0.289	3.523
	0.46	0.089	1.33	57.08	0.325	3.501
TBP	0.38		0.93	48.19	0.234	3.274
	0.62	_b	1.14	53.28	0.326	3.255
	0.75		1.26	55.75	0.369	3.252

<sup>a</sup>  $(D_m)$  Distribution ratio in presence of mixed extractant; SC, synergistic coefficient, SC = log $[D_m/(D_0 + D_S)]$ ;  $\beta = (D_m - D_0)/(D_0[S])$ , apparent formation constant.

<sup>b</sup> Pure TBP extracts Au(III) under these conditions negligibly.

**Table 4.** Equilibrium constants for binary and ternary systems

Au(III)—ligand system $\log k$	Ternary systems		
	donor	logK	$\log K_{\rm S}$
-2.27	TBPO	0.975	3.245
	TPPO	0.825	3.095
	TBP	0.545	2.815

concentrations will correspond to the number of ligand molecules in the mixed complex. The adduct formation reaction in the organic phase can be presented as

$$[AuA_3]_{org} + S_{org} \rightleftharpoons [AuA_3 \cdot S]_{org}.$$
 (6)

Correspondingly,

$$\log K_{\rm S} = \log K - \log k,\tag{7}$$

where  $K_{\rm S}$  is the adduct formation constant in the organic phase.

The experimental data on synergistic effects of each of the two phosphine oxides and TBP on the extraction of gold with HA are given in Table 3. As can be seen, in all the cases the extraction percentage and synergistic coefficient (SC) increase with the donor concentration, showing enhanced replacement of water molecules from the metal environment. The synergistic coefficient and apparent formation constant of the ternary complex are defined as

SC = log 
$$[D_m/(D_0 + D_S)]$$
,  
 $\beta = (D_m - D_0)/(D_0[S])$ .

As seen from Table 3, SC and  $\beta$  decrease in the order TBPO > TPPO > TBP, in accordance with the trend in the electronic effects of substituents. The equilibrium constants for the binary and ternary systems are given in Table 4. They show that fairly stable adducts are formed in chloroform.

Effect of temperature. The extraction of Au(III) from aqueous HCl with a mixture of *N*-(thioacetyl)benzamide and phosphine oxides or TBP was also studied in relation to temperature (25–45°C, Fig. 5), and thermodynamic functions (enthalpy of formation  $\Delta H^0$ , entropy of formation  $\Delta S^0$ , free energy of formation  $\Delta G^0$ ) were calculated using the van't Hoff equation [26, 27]. The results are given in Table 5.

The experimental data were processed by linear regression analysis. The data clearly show that the extraction of gold with HA only is endothermic ( $\Delta H^0 > 0$ ). When a cation is transferred from an aqueous medium into an organic phase through an ion exchange– complexation mechanism, the net enthalpy and entropy associated with the extraction will be mainly due to two opposing processes: (1) dehydration of the extracted cation and hydration of the exchanged protons; (2) metal coordination by the organic ligand and deprotonation of the ligand [28]. The positive entropy



**Fig. 5.** Temperature dependence of the equilibrium constants for the binary and ternary systems. Donor: (1) none, (2) TBPO, (3) TPPO, and (4) TBP.

change  $\Delta S^0$  in the binary extraction system is apparently due to dehydration of the gold ion before its extraction into the organic phase with the release of water molecules. The dehydration of the metal cation also involves a positive enthalpy change ( $\Delta H^0 > 0$ ) as a result of the cleavage of the ion-water bonds. The positive entropy change ( $\Delta S^0 > 0$ ) can be associated with complete dehydration of the metal cation whose effect is not compensated by the simultaneous hydration of the equivalent amount of H<sup>+</sup> ions. Positive entropy change generally contributes to the enhanced stability of chelates [27]. Thus, the binary extraction proceeds nonspontaneously in the forward direction, endothermally with entropy gain.

All the thermodynamic functions of the synergistic extraction process appeared to be negative in the experimental temperature range. The negative enthalpy values for the adduct formation show that the adduct containing TBPO is the most favorable among the three donor systems, in agreement with the electron-donor power of the phosphoryl oxygen atom. The higher the donor power, the higher the probability of formation of an additional bond with the gold atom. In this case, the negative enthalpy change is expected, because the adduct formation is not accompanied by bond cleavage. The negative values of  $\Delta S^0$  suggest a decrease in the randomness in the same order TBP–

 Table 5. Thermodynamic functions of the binary [Au(III)–ligand] and ternary [Au(III)–ligand–donor] extraction systems

Donor	$\Delta H^0$ , kJ mol <sup>-1</sup>	$\Delta S^0$ , J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^0$ at 27°C, kJ mol <sup>-1</sup>
_	$22.81 \pm 0.2$	$31.52 \pm 0.5$	$13.35 \pm 0.1$
TBPO	$-19.32 \pm 0.1$	$-44.64 \pm 0.1$	$-5.93 \pm 0.4$
TPPO	$-12.26 \pm 0.2$	$-24.36 \pm 0.3$	$-4.95 \pm 0.2$
ТВР	$-7.22 \pm 0.3$	$-13.32 \pm 0.2$	$-3.23\pm0.2$

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TPPO–TBPO. Thus, the adduct formation reaction occurs spontaneously, exothermally, with the entropy loss. The negative  $\Delta H^0$  and  $\Delta S^0$  values are characteristics of outer-sphere complexation [26]. Thus, the synergistic effect of the donor is due to expansion of the coordination sphere of an Au(III) atom, which accommodates an additional electron pair donated by organophosphorus compounds.

**IR spectra.** The IR data [24] clearly support the formation of [AuA<sub>3</sub>·S] in the organic phase. The ligand is bound to the metal ion through the C–S bond, as indicated by the shift of  $v_{C=S}$  from 1152 cm<sup>-1</sup> in the free ligand spectrum to 1141 cm<sup>-1</sup> in the spectrum of the complex. A new band appears at 1596 cm<sup>-1</sup>, absent in the free ligand spectrum and assignable to  $v_{C=N}$ ; its appearance is due to deprotonation of the N atom upon complex formation in the organic phase. Similarly,  $v_{P=O}$  has shifted from 1144 to 1120 cm<sup>-1</sup>, suggesting bonding of phosphine oxide molecules with the metal chelate.

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