# THE SYNERGISTIC MECHANISM OF SOLVENT EXTRACTION OF GOLD IN HCl MEDIA WITH TOA AND TOPO

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**Abstract**  The mechanism of synergistic extraction of gold in HCl media was researched with tri-n-octyl amine(TOA) and tri-n-octyl phospine oxide(TOPO). It was determined that the composition of synergistic extract is (TOAHTOPO)$AuCl_4$; the constant of synergistic extracting equilibrium is $10^{9.20}$; and the synergistic reaction is exothermic with $-17.187$ kJ/K·mol of $\Delta H_{298}$. The extraction mechanism was also studied by the IR-spectra and UV-spectra. It is found that the extraction mechanism belongs to ion-association type.

**Key words**  gold; synergistic extraction; hydrochloric acid media; mechanism of extraction

Chlorination in aqueous solution is one of the major methods in hydrometallurgy of gold, especially the extraction of gold from anode slime. Although there are many ways of extracting gold from chlorination solution, gold can not be recovered effectively from low concentration feed solution.

Solvent extraction is an effective method for recovery of gold from chlorination solution. Tri-n-octyl amine is an excellent extractant, and trioctyl phosphine oxide(TOPO) is a synergistic extractant for amine thermodynamically. It was reported that TOA and TOPO were used to extract gold from HCl media respectively[1~4]. And there were some researches on synergistic extraction of gold with TOA and TOPO in sulfuric acid media or thiourea-containing $H_2SO_4$ media[1,5].

In this work, the mechanism of synergistic extraction is studied by using TOA and TOPO as extractants, and IR and UR spectra analyses of the related systems.

## 1  EXPERIMETAL

### 1.1  Reagent

Tri-n-octyl amine, Germany made, purity > 95%.

Tri-n-octyl phosphine oxide: E. Merk reagent, A. R.

Gold solution: Gold powder of 99.99% was dissolved by aqua regia. The solution containing 1.0 g/L gold in HCl media, was diluted to required concentration when used.
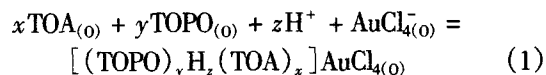
### 1.2  Procedure

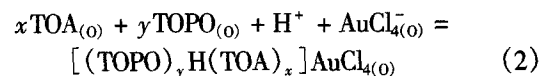The feed solution was prepared by 1.0 g/L gold solution, HCl and LiCl solutions. Organic phase was made by dissolving TOA and TOPO in $CCl_4$ according to required concentrations respectively. Mix the aqueous phase and organic one in separatory funnel, and vibrate for a certain time. Separate the aqueous phase from organic one. Analyse gold concentration of the raffinate by spectrometric method . 0 . 0 0 5 mol / L TOA and 0 . 0 0 5 mol/L TOPO organic phase and its loaded phase are analyzed by Inferred analyzer. Ultraviolet spectra of feed solution of 50 mg/L gold and loaded organic phase are made in UV-3000 spectrometer.

## 2  RESULTS AND DISCUSSIONS

Generally reaction for extraction of gold from hydrochloric acid media by TOA and TOPO can be expressed as follows:

$$x\text{TOA}_{(o)} + y\text{TOPO}_{(o)} + z\text{H}^+ + \text{AuCl}_{4(o)}^- =$$
$$[(\text{TOPO})_y\text{H}_z(\text{TOA})_x]\text{AuCl}_{4(o)} \qquad (1)$$

Since the coefficient of $\text{H}^+$ should be one according to the principle of charge balance the equation can be rewritten as:

$$x\text{TOA}_{(o)} + y\text{TOPO}_{(o)} + \text{H}^+ + \text{AuCl}_{4(o)}^- =$$
$$[(\text{TOPO})_y\text{H}(\text{TOA})_x]\text{AuCl}_{4(o)} \qquad (2)$$

The relationship between distribution and equilibrium constant ($K_{ex,s}$) of reaction (2) can be expressed as follows:

$$\lg D_s = \lg K_{ex,s} + y\lg c(\text{TOPO})_0 +$$
$$x\lg c(\text{TOA})_0 + \lg c(\text{H}^+) \qquad (3)$$

Here $D_s$ denotes distribution ratio contributed by synergistic extraction. It has the following expression:

$$D_s = D_T - (D_N + D_P)$$

$D_T$ is the total distribution ratio, and $D_N$ and $D_P$ are distribution ratios contributed by TOA and TOPO in TOA + TOPO - CCl$_4$ system respectively. The dependence of the mole fraction of TOA or TOPO ( $x$ ( TOA ) or $x$(TOPO)) on the extraction of gold is shown in Fig. 1 under the following conditions: $c^0$(Au( Ⅲ )) 100 mg/L, $c$(Cl$^-$ ) = 6.0 mol/L, O/A = 1, $c$ (H$^+$ ) = 0.7 mol/L and temperature 13.5 ℃.
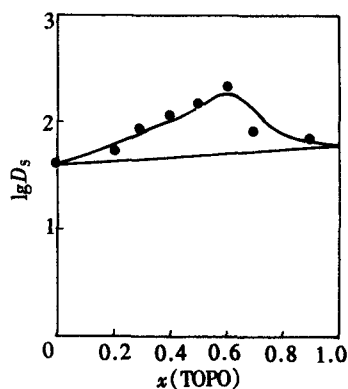


Fig. 1 Synergistic extraction diagram of TOA + TOPO - CCl$_4$ system

From Fig. 1 it can be seen that the distribution $D_S$ reaches its maximum when $x$ (TOPO) is equal to 0.6; lg$D_s$ increases gradually when $x$(TOPO) is less than 0.6 and lg$D_S$ decreases sharply at $x$(TOPO) > 0.6. In order to investigate synergistic extraction, the following experiments are carried out at $x$(TOPO) = 0.5.

## 2.1 Effect of Acidity

The fixed conditions are as follows: ratio of organic phase to aqueous one (O/A) 1:1, $c^0$(Au( Ⅲ )) = 100 mg/L, $c$(Cl$^-$ ) = 6.0 mol/L, 0.00075 mol/L TOA and 0.00075 mol/L TOPO in CCl$_4$ phase. The results are shown in Fig.2.

From Fig . 2 it is shown that lg $D_S$ increases as lg$c$(H$^+$ ) increases and lg$D_S$ is linear with lg$c$ (H$^+$ ). The slope of straight line in Fig.2 is 1.065. Therefore it
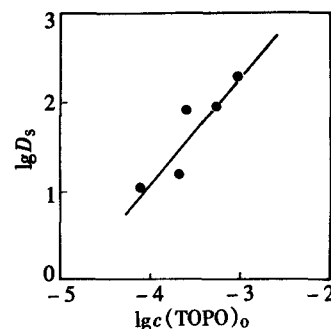
can be reckoned that $z$ value in equation (2) is 1.



Fig. 2 The relationship between lg$D_s$ and lg$c$(H$^+$ )

## 2.2 Equilibrium Constant and Effect of Extractant Concentration on Synergistic Distribution

The fixed conditions are as follows: the ratio of organic phase to aqueous one 1, temperature 13.5 ℃, initial Au concentration in aqueous phase 100 mg/L, concentration of Cl$^-$ 6.0 mol/L and acidity 0.7 mol/L.

If extraction reaction proceeds by equation (2), the concentrations of extractants in equilibrium are as follows[6]:

$$c(TOA)_0 = c^0(TOA) - xc^0(Au( Ⅲ ))(D_N + D_S)/(D_T + 1)$$
$$c(TOPO)_0 = c^0(TOPO) - yc^0(Au( Ⅲ ))(D_P + D_S)/(D_T + 1)$$

For different values of $x$ and $y$ , $c$ ( TOA )$_0$ and $c$(TOPO)$_0$ were calculated out. It is found that if $x$ or $y$ is larger than 1, $c$(TOA)$_0$ and $c$(TOPO)$_0$ have negative values. Only when $x$ and $y$ are all 1, the equilibrium concentrations of the extractant are positive ones. The results are presented in Table 1.

Effect of TOA on gold extraction at $c^0$(TOPO) = 0.001 mol/L is shown in Fig. 3. And effect of TOPO on gold extraction at $c^0$(TOA) = 0.001 mol/L is shown in Fig. 4.

Table 1 Extraction of gold at different extractant concentrations in TOA + TOPO - CCl$_4$ system

| $c^0$(TOA)/mol·L$^{-1}$ | $c^0$(TOPO)/mol·L$^{-1}$ | lg$c$(TOA)$_0$ | lg$c$(TOPO)$_0$ | $D_N$ | $D_P$ | lg$D_S$ | lg$K_{ex,s}$ |
|---|---|---|---|---|---|---|---|
| 0.00032 | 0.0010 | -4.27 | -3.25 | 0.43 | 4.0 | 0.71 | 9.16 |
| 0.0005 | 0.0010 | -3.77 | -3.25 | 1.06 | 4.0 | 0.91 | 8.86 |
| 0.0007 | 0.0010 | -3.61 | -3.27 | 2.81 | 4.0 | 1.62 | 9.44 |
| 0.0010 | 0.0010 | -3.27 | -3.24 | 10.91 | 4.0 | 1.74 | 9.19 |
| 0.0014 | 0.0010 | -3.04 | -3.18 | 65.67 | 4.0 | 2.11 | 9.27 |
| 0.0010 | 0.00032 | -3.28 | -4.10 | 10.905 | 0.29 | 1.02 | 9.34 |
| 0.0010 | 0.0005 | -3.28 | -3.69 | 10.905 | 0.74 | 1.20 | 9.10 |
| 0.0010 | 0.0007 | -3.29 | -3.59 | 10.905 | 1.44 | 1.89 | 9.70 |
| 0.0010 | 0.0010 | -3.29 | -3.26 | 10.905 | 4.00 | 1.94 | 9.42 |
| 0.0010 | 0.0014 | -3.27 | -3.03 | 10.905 | 16.86 | 2.24 | 9.47 |

It can be seen from Fig. 3 that $\lg D_S$ has straight line with $\lg c(TOA)_0$. The line has the slope of 1.1690 and the intercept(A) of 5.6182. As a result the $x$ value of equation (2) can be considered as 1.
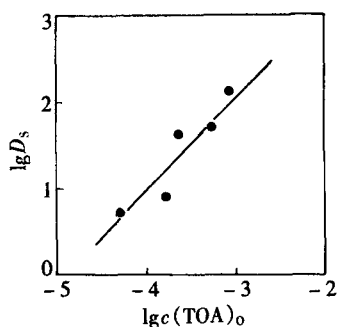


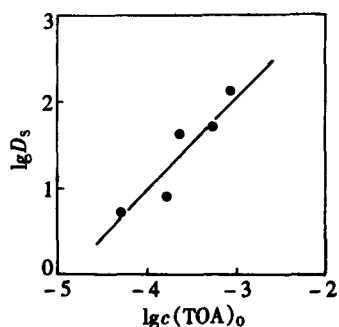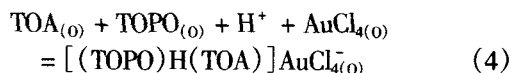**Fig. 3** The relationship between $\lg D_s$ and $\lg c(TOA)_0$



**Fig. 4** The relationship between $\lg D_s$ and $\lg c(TOPO)_0$

It can be seen from Fig. 4 that $\lg D_S$ is linear with $\lg c(TOPO)_0$ with the slope of 1.1673 and the intercept (A) of 5.7832. The $y$ value of equation (2) is approximately 1.

Therefore equations (2) and (3) can be rewritten as:

$$TOA_{(o)} + TOPO_{(o)} + H^+ + AuCl_{4(o)}$$
$$= [(TOPO)H(TOA)]AuCl_{4(o)}^- \qquad (4)$$
$$\lg D_s = \lg K_{ex,s} + \lg c(TOPO)_0 + \lg c(TOA)_0 + \lg c(H^+) \qquad (5)$$

There are two ways to obtain equilibrium constants of synergistic extraction. The constants can be calculated by Xu Guangxian method[6] with $\lg K_{ex,s}$ average value of 9.30 as shown in Table 1 . By the intercepts in Fig . 3 and Fig.4 the values of $\lg K_{ex,s}$ can be obtained as 9.18 by $\lg K_{ex,s} = A - \lg c(H^+) - \lg c(TOPO)_0$ at constant $c(TOPO)_0$ and as 9.21 by $\lg K_{ex,s} = A - \lg c(H^+) - \lg c(TOA)_0$ at constant $c(TOA)_0$. The average value of $\lg K_{ex,s}$ by the intercept is 9.20. Compared with the value by Xu method only 0.1 error exists. Moreover the equilibrium constant of extraction by TOA is $10^{8.35}$ and that by TOPO is $10^{8.29}$.

## 2.3 The Effect of Temperature

The equilibrium constant can be changed to some extent due to the change of temperature. From the relationship between the equilibrium constant of extraction and $\Delta H$, the relation of $\lg D_s$ to $\Delta H$ can be described as:

$$\lg D_S = -\Delta H/19.146T + C$$

where C is a constant.

Fig . 5 is the relationship between $\lg D_s$ and $1/T$ at $c^0(Au(\text{III})) = 100$ mg/L, $c(Cl^-) = 6.0$ mol/L, $c(H^+) = 0.7$ mol/L, $A/O = 1.0$, $c_T = 0.002$ mol/L , the ratio of TOA to TOPO = 1:1.

From Fig.5 it is found that there exists the linear relation between $\lg D_s$ and $1/T$. The straight line has the slope of 0.8977, $\Delta H_{298}$ being $-17.187$ kJ/K·mol.
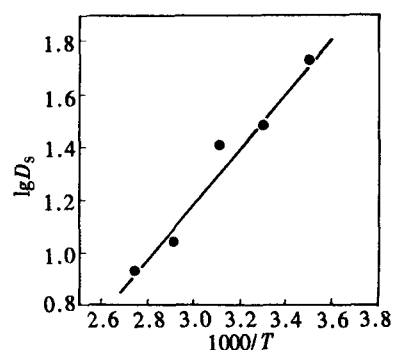


**Fig. 5** The relation of $\lg D_S$ to $1/T$

## 2.4 IR and UR Spectra

In order to investigate the behavor of $AuCl_4^-$ during the extraction , the UR spectra of the feed solution of 5 0 mg/L Au,6.0 mol/L $Cl^-$ and 0.5 mol/L $H^+$ and loaded $CCl_4$ phase were made, as shown in Fig. 6.

In the feed solution there exists characteristic absorption of $AuCl_4^-$ at 315 nm. After the extraction the characteristic absorption will shift to near 325nm. The small difference of the characteristic absorption is ascribed to the adoption of solvents in related systems, where the solvent of the feed solution is water and that of loaded organic phase is $CCl_4$. The enhancement for intensity of the characteristic absorption in loaded organic phase is due to its relatively high gold concentration. These results show that there is no electron transference during the extraction, that is, when gold is extracted into organic phase it still exists as $AuCl_4^-$ .

In order to investigate the behavior of TOA and TOPO during the extraction IR spectra of 0.005 mol/L TOA and 0.005 mol/L TOPO organic phase and its loaded phase are made, as shown in Fig.7.
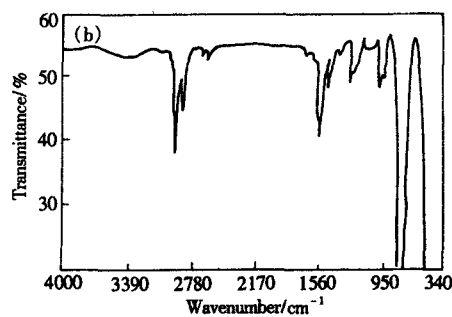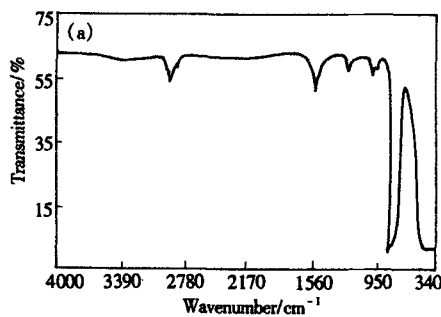
There exists an obvious absorption peak near 2 7 8 0 $cm^{-1}$ which is the stretching vibration of $CH_2$ in amido group. It is shown that there is amine in organic phase.
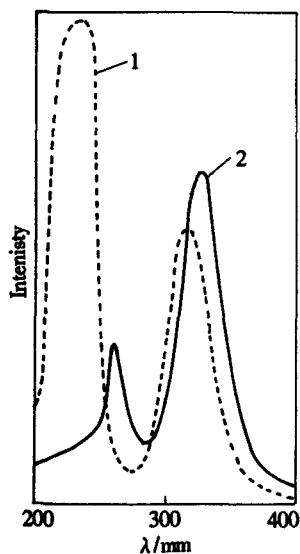
1—Feed solution; 2—Loaded organic phase

**Fig. 6**  UR spectra of TOA + TOPO – CCl₄ systems

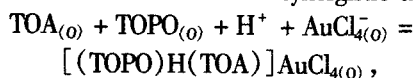However after the extraction there appear two new stretch-

ing vibrations of $H^+$ in aminate at $2750 \sim 2250$ cm$^{-1}$, as shown in b of Fig.7. This result shows that there exists a protonation reaction between $H^+$ and N in TOA to form $R_3NH^+$, which is the same as that of TOA—CCl₄ system. On the other hand there is no obvious change near $P=O$ group vibration peak($1150$ cm$^{-1}$) after the extraction, which is also the same as that of TOPO—CCl₄ system. But it can not be concluded that there is no reaction between $H^+$ and $P=O$ group in TOPO because the action of $H^+$ to $P=O$ group is overlapped by the disturbing peak of solvent CCl₄. From the analysis of the spectra it can be reckoned that there might exist two ways for the extraction of gold. One way is that, TOA and TOPO share the same $H^+$ to form TOAHTOPO$^+$, then TOAHTOPO$^+$ is combined with AuCl₄$^-$ to form the extract of $(TOAHTOPO)^+ AuCl_4^-$. Another way is that before the action between $H^+$ and $P=O$ group takes place the protonation of TOA will proceed to form TOAH$^+$, then TOAH$^+$ reacts to AuCl₄$^-$ to form TOAH$^+$ AuCl₄$^-$. TOAH$^+$ AuCl₄$^-$ will continue to react with TOPO to form $(TOAH^+ AuCl_4^-)$TOPO, which is more easily soluble in the organic phase.



(a) Phase of TOA + TOPO – CCl₄;  (b) Loaded phase of TOA + TOPO – CCl₄

**Fig. 7**  IR spectra of organic phase and loaded one(TOA 0.005 mL/L; TOPO 0.005 mL/L)

## 3  CONCLUSIONS

1) The overall reaction of the synergistic extraction is

$$TOA_{(o)} + TOPO_{(o)} + H^+ + AuCl_{4(o)}^- =$$
$$[(TOPO)H(TOA)]AuCl_{4(o)},$$

with the composition of the synergistic extract being $[(TOPO)H(TOA)]AuCl_{4(o)}$.

2) It is determined that the equilibrium constant of the synergistic extraction is $1\,0^{9.20}$, with $-17.187$ kJ/K·mol of $\Delta H$.

3) From the analysis of IR spectra and UR one, it is reckoned that the extraction belongs to ion association type.

## References

1  Shui Chenjing, Yang Tianzu, Bin Wanda. Review on advance in solvent extraction of gold. Gold(in Chinese), 1998, 19(3):35 ~ 38

2  Wang Wenming. Extraction of gold with TOA and its stripping. Gold(in Chinese), 1987, 8(4):52 ~ 55

3  Tocher M I, Whitney D C, Diamond R M. The extraction of acids by organic solvent, IV Tributyl phosphate and Trioctyl phosphine oxide — HAuCl₄ and HAuBr₄. J of Phys Chem, 1964, 68(2):368 ~ 374

4  Shui Chenjing, Yang Tianzu, Bin Wanda. The solvent extraction of gold from hydrochloric acid media by TOA. Precious Metals(in Chinese), 1998,19(2):34 ~ 39

5  Niinae M, Oboso A. Synergistic extraction of gold from sulfuric acid solution containing thiourea. Nippon Kinzoku Gakkaishi(in English), 1991, 55(8):867 ~ 873

6  Xu Guangxian. The principle of solvent extraction chemistry(in Chinese). Shanghai: Shanghai Science and Technology Press, 1984.138 ~ 176