

Liquid–Liquid Extraction of Silver (I) with 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone into Cyclohexene from Nitrate Medium in Presence of Neutral Oxygen Donor Compounds.

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Abstracts: The extraction behaviour of Ag (I) from an aqueous nitrate medium employing 2-hydroxy-1-naphthaldehyde thiosemicarbazone in cyclohexene has been investigated in presence of several donors like, tri-octyl phosphine oxide (TOPO), tri-butyl phosphine oxide (TBPO) and tri-butyl phosphate (TBP) at pH 3.0 adopting radiotracer technique. The synergism was found in presence of neutral donors due to the formation of the adduct [Ag (A).(S)] in cyclohexene (S denotes several donor). The overall equilibrium constant for each of the three ternary complexes and also for binary system were calculated from extraction distribution data. It was found that the extent of extraction of Ag (I) in organic phase for the binary complex increased with increase in temperature, but for ternary complexes reverse order were found. The temperature dependence of the equilibrium constants was investigated in order to evaluate the thermodynamic parameters like enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°).

Key words: Silver extraction; Synergistic effect organophosphorus donors; 2-hydroxy-1-naphthaldehyde thiosemicarbazone.

Introduction

The liquid-liquid extraction of silver (I) has long been studied from nitrate or chloride media, and various extractants have been suggested¹⁻⁴. It was suggested that the carbonyl compound extractants were found to selectively extract silver ion over other soft metal ions from highly acidic solution⁵⁻⁶. According to the hard-soft acid-base (HSAB) concept⁷, chelating ligand have hard donor sites, being capable of complexing with hard metals while some have soft donor sites to form stable adduct with soft metal. Since sulfur-containing extractants (soft bases) selectively extract metals classified as soft acids, e.g., Au, Ag, Pd, and Pt, but do not extract base metals. A significant number of efficient sulfur reagents have been proposed for use in

the extractive separation of soft metal ;), such as thioamide derivative⁸, thiourea derivatives⁹ dialkyl (aryl) sulfides¹⁰, mercaptobenzothiazole¹¹ and thiourea derivatives containing N-substituted alkylthiourea¹². Preston and du Preez¹³ studied the effect of some aliphatic S-donor ligands, including alkanethiols (RSH), dialkyl sulfides (RSR) and dialkyl disulfides (RSSR) on the solvent extraction of Cd and Zn with di-isopropylsalicylic acid (DIPSA). Preston¹⁴ investigated the effect of the S-donor ligands, including trialkyl thiophosphates [(RO)₃PS] and trialkylphosphine sulphides (R₃PS), as synergists, on the extraction of Cd and Zn with carboxylic acid extractants in xylene. Teresa Flor¹⁵ studied the thermodynamic characterization of the liquid-liquid extraction of silver by acyclic dithia benzene

derivatives in chloroform solution. In order to develop the extraction process, elucidation of the synergic extraction behavior of divalent metals is one of the important subjects has been extensively studied. This phenomenon "synergism" is understood to be an increase in the lipophilicity of the extracted metal complexes arising from the replacement of residual water in the inner coordination sphere or to occupy open coordination sites by neutral electron donors, called synergists. Furthermore, synergistic extraction of metal ions has various advantages over ordinary solvent extraction system, such as enhancement of extractability, widening the optimum extraction pH range, stabilization of extracted species by forming an adduct¹⁶. In a recent work, synergistic extraction of silver (I) from aqueous nitrate medium with different combination of ligands has been reported. Yasunobu Ohmiya and Tatsuya Sekine¹⁷ studied the extraction behaviour of silver from aqueous sodium nitrate medium with 2-thenoyltrifluoroacetone (HTTA) and 4-isopropyltropolone (HIPT) in the absence and presence of tetrabutylammonium ions (TBA⁺), into chloroform solvent. Those authors previously studies¹⁸ the synergistic extraction of silver from nitrate medium into chloroform in presence of some π -donor and n-donor. Vesna Gasperov¹⁹ observed the synergistic extraction of Ag(I) from nitrate medium using a mixture of with 1,4,8,11-tetrabenzyl-1,4,8,11-tetraazacyclodecane and lipophilic organic carboxylic acid via the formation of Host-guest assemblies between those ligands as well as metal ion into chloroform. Much attention has been paid to the synergistic extraction of metal ion especially in combination chelating extractant with neutral organophosphorus donor into organic solvent²⁰⁻²¹.

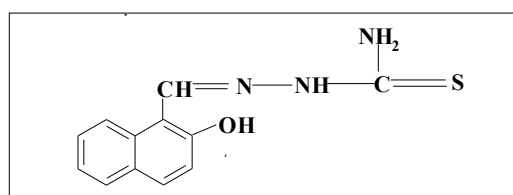
In the present work we have synthesized from the knowledge of (HSAB) concept a new sulphur donor sites chelating ligand 2-hydroxy-1-naphthaldehyde thiosemicarbazone (TSN) for the extraction of Ag (I) into cyclohexene solvent from aqueous nitrate medium. And synergistic effect was study by the addition of nutral organophosphorus donor tri-octyl phosphine oxide (TOPO), tri-butyl phosphine oxide (TBPO), tributyl phosphate (TBP), into organic phase. The aim of the work is to determine the synergistic coefficient, equilibrium constant and different thermodynamic parameter of the both binary and ternary extracted complexes.

EXPERIMENTAL

Reagents and solutions:

The extractant 2-hydroxy-1-naphthaldehyde thio semicarbazone was synthesized by the reaction between 2-hydroxy naphthaldehyde (BDN) and thiosemicarbazide (SRL) in ethyl alcohol medium²²,

were obtained from Aldrich, USA. The product was recrystallised and characterized by elemental analysis, IR and NMR data. The donor reagents used in this work e.g tri-octyl phosphine oxide (TOPO), tri-butyl phosphine oxide (TBPO), tri-butyl phosphate (TBP), were also collected from Aldrich; USA. The solvents were purified by standard procedures. All other reagents used were of A.R. grade. A stock solution of silver was prepared by dissolving AR AgNO₃ in deionised water and a working stock was prepared by appropriate dilution. In order to spike the solution, an appropriate volume of stock solution of Ag (I) was mixed, with few drops of tracer solution containing, ^{110m}Ag as AgNO₃ supplied by BRIT, India and finally made up to the mark.



Scheme-I. Scheme of the chemical formula 2-hydroxy-1-naphthaldehyde thiosemicarbazone.

Instruments:

Microanalysis of carbon, hydrogen and nitrogen content of the synthetic ligand were achieved in a Perkin-Elmer 2400 CHNS-O elemental analyzer. Infrared spectra of ligands and adduct complexes were recorded in 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 γ -ray spectrometer coupled with a well-type NaI (T1) detector of Nucleonix, India make was used for radio-activity measurement. The radioisotope ^{110m}Ag was assayed by its 667 keV photopeak.

Extraction and analytical procedures:

In the general extraction procedure, 5 ml aqueous solution of AgNO₃ containing ~ 150 μ g spiked Ag(I), and adjusted to a pH 3.00 was extracted with equal volume of cyclohexene solution of chelating ligand for a period of 30 minutes in a mechanical shaker. Ionic strength of the solution was kept fixed by using 0.50 M KNO₃. For synergistic study, organic phase was mixed with appropriate donor reagent of desired concentration. After the equilibration, two phases were separated and radio-activities of equal volumes of both of the two phases were measured. Distribution Coefficients (D) were computed from,

$$D = \frac{\text{Radioactivity in organic phase}}{\text{Radioactivity in aqueous phase}}$$

Material-balance in the extraction was checked from the counts of two phases separately.

RESULTS AND DISCUSSION

Effect of equilibration time:

Preliminary studies on the extraction of Ag (I) by 2-hydroxy-1-naphthaldehyde thiosemicarbazone in cyclohexene show that the two phase reaction is fairly rapid and the equilibrium is reached within 30 minutes. The increase of the time of equilibration does not affect the extraction equilibrium.

Effect of organic diluents:

It is well known that the diluent plays an important role in solvent extraction by affecting of the extraction process²³. Some organic solvent like Carbon

tetrachloride (CCl₄), chloroform (CHCl₃), xylene, toluene, benzene, cyclonexene and nitrobenzene were chosen to study the effect of diluents extraction of upon the Ag (I) from aqueous nitrate solution. It has been observed that at a fixed concentration of TSN and donor by keeping pH fixed at 3.0, cyclohexene performs better compared to other diluents. The trends are as follows: cyclonexene >CCl₄> benzene > xylene> toluene> CHCl₃>Nirtobenzene in Table: 1. A considerable improvement of the extraction of Ag (I) by extractant was brought about by changing diluent from polar to non-polar nature. The drive of water molecules in the organic phase is more significant in polar than non-polar²⁴. As a result, when cyclohexane was used as a diluent, the extraction was clearly improved. This improvement may be explained by the fact that the water molecules which accompany the metal complex in organic phase are possibly raised.

Table: 1. The Extraction of Ag(I) with 2.503×10^{-2} mol.dm⁻³ of 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone in Different Diluents from Aqueous Nitrate Medium of Constant Ionic Strength at pH 3.0.

Diluents	Dielectric constant (ϵ)	Distribution coefficient (Do)	(%) Extraction
Cyclohexene	2.01	8.43	89.39
Carbon tetrachloride	2.22	5.64	84.93
Benzene	2.26	4.58	84.81
Xylene	2.35	2.47	71.21
Toluene	2.36	1.12	52.84
Chloroform	4.62	0.96	48.97
Nitrobenzene	34.8	0.41	29.08

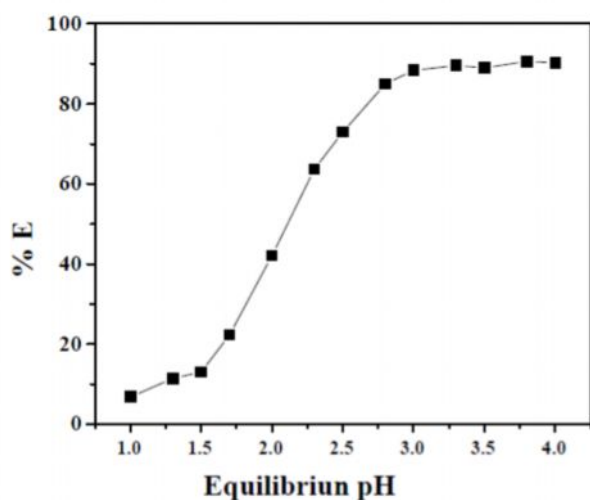


Figure-1: % E vs. Equilibrium pH of the aqueous nitrate solution for the extraction of Ag(I) with 2.502×10^{-2} M 2-hydroxy-1-naphthaldehyde thiosemicarbazone in cyclohexene.

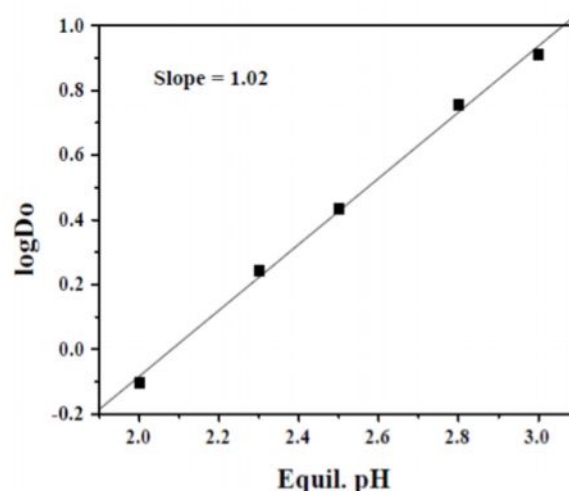


Figure- 2: log Do vs. pH of the aqueous nitrate solution for the extraction of Ag(I) with 2.502×10^{-2} mol.dm⁻³ 2-hydroxy-1-naphthaldehyde thiosemicarbazone in cyclohexene.

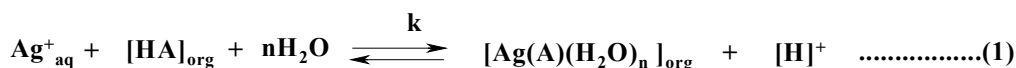
Effect of equilibrium pH:

It is known that the acidity of the aqueous solution strongly affects the efficiency of the metal extraction by chelating extractants. The extraction of Ag (I) as a function of equilibrium pH in cyclohexene has been studied over the range of 1.0-4.0 equilibrium pH using $2.503 \times 10^{-2} \text{ mol.dm}^{-3}$ of extractant. Extraction was only 15 % at ~1.5 equilibrium pH and increased steadily with the increase in equilibrium pH given in **Figure-1**. The extraction was quantitative in the range 1.76-3.0. The plot of logD_o vs. equil. pH (in the pH range 2.0-3.0) gave a straight line with a slope ~ 1 in **Figure -2** indicating that only one H⁺ ion was liberated from the extractant on complexation of Ag(I) with TSN to give extractable species in the organic phase. An optimum equilibrium pH of 3.0 was selected for the further experiments. [D_o = distribution co-efficient in presence of only extractant]

Extraction of Ag (I) with 2-hydroxy-1-naphthaldehyde thiosemicarbazone (HA):

Extraction of Ag (I) from nitrate medium was investigated using cyclohexene as a diluent. The concentration of ligand was varied from $2.5 \times 10^{-2} \text{ mol.dm}^{-3}$ to $0.35 \times 10^{-3} \text{ mol.dm}^{-3}$ in cyclohexene. The percentage of extraction was found to increase with increase in ligand concentration at fixed pH 3.0. At higher concentration of ligand, effective stripping of the water molecules take place from the hydrated silver ion sphere by the ligand, rendering the species much more organophilic in nature. The linear plot of logD_o against concentration of ligand with a slope ~ 1 given in Figure- 3 indicating one molecule of ligand (HA) is involved in the extraction of silver according to Equation (1).As the ligand is bidentate in nature, only one molecule of ligand is sufficient to balance the charge of monovalent metal ion.

The overall binding extraction is described as,



The distribution coefficient is defined by,

$$D_o = \frac{[\text{Ag}(\text{A})(\text{H}_2\text{O})]_{\text{org}}}{[\text{Ag}^+]_{\text{aq}}} \dots\dots\dots(2)$$

Thus equilibrium constant (k) for binary extraction is related to the distribution Co-efficient by,

$$\log k = \log D_o - \log[\text{HA}] - \text{pH} \dots\dots\dots(3)$$

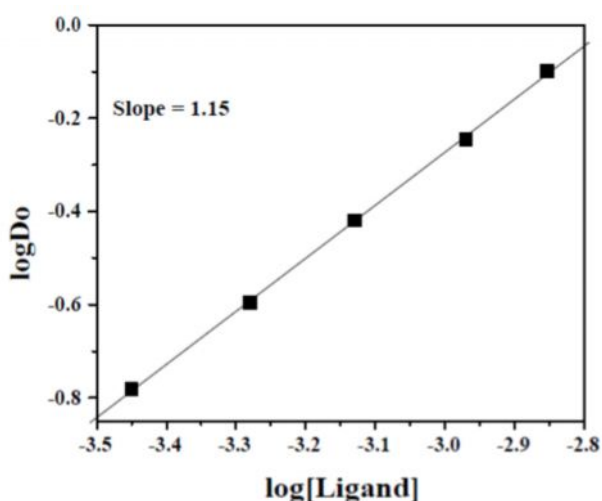


Figure-3: Variation of Ag(I) distribution ratios with 2-hydroxy-1-naphthaldehyde thiosemicarba zone at equilibrium pH-3.0 values of the aqueous nitrate solution.

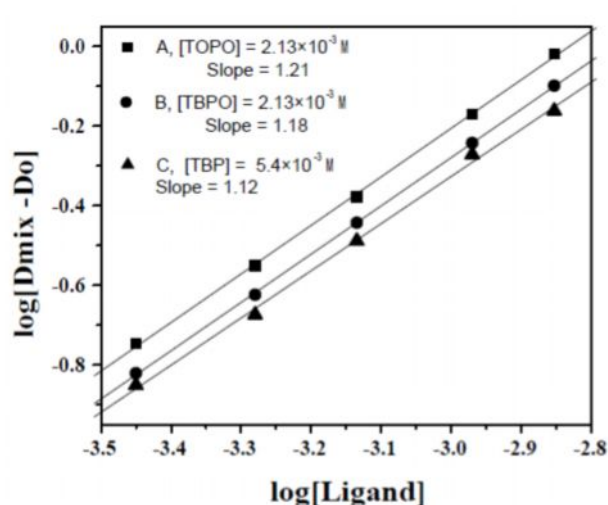


Figure-4: The plot of log[Dmix – D_o] vs log[Ligand] in synergistic extraction of Ag(I) from aqueous nitrate medium.

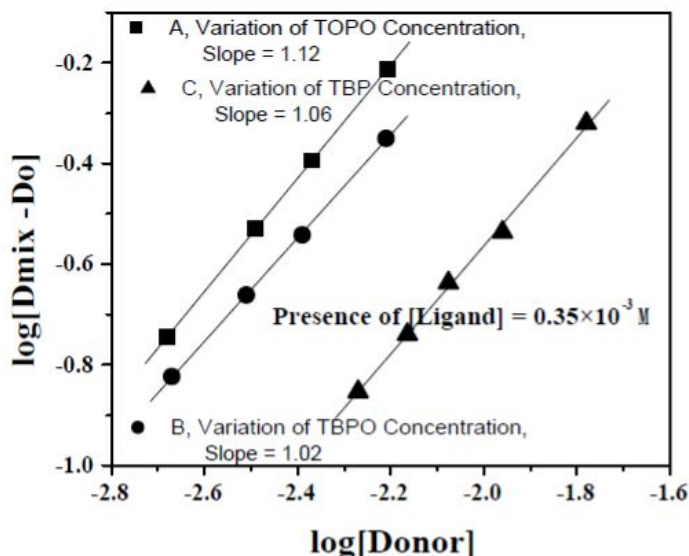


Figure- 5: The plot of log[Dmix – Do] vs log[Donor] in synergistic extraction of Ag(I) by 2-hydroxy-1-naphthaldehyde thiosemicarbazone with fixed concentration [0.35×10⁻³ mol.dm⁻³] from aqueous nitrate solution in presence of different concentration of donors at pH 3.0 into cyclohexene solvent

Extraction of Ag (I) with 2-hydroxy-1-naphthaldehyde thiosemicarbazone (HA) in presence of phosphine oxide and tributyl phosphate:

The distribution ratio of Ag (I) extracted with HA increases by the addition of different organophosphorous compounds. This is attributed to the formation of a more lipophilic adduct with these donors. In the ternary extraction system, the log[Dmix –Do] vs. log [HA] plots at fixed concentration of donor and fixed pH of aqueous phase yielded slope of

~1 in Figure- 4. while the log[Dmix –Do] vs. log[donor] plots at fixed concentration of ligand and fixed pH of aqueous phase showed straight line behavior with a slope also ~1 in Figure- 5. suggesting the composition of the extracted species of the type Ag(A).(S).The overall reaction of the generally accepted synergistic extraction of silver ions is given by Equation (4) where one molecule of ligand and one molecule donor (S) are present in the extracted adduct.

Hence, ternary adduct formation may be described as,



Obviously, Equilibrium constant (K) is shown by

$$K = \frac{[Ag(A).(S)]_{org} [H]^+_{aq}}{[Ag]^+_{aq} \cdot [HA]_{org} \cdot [S]_{org}} \dots\dots\dots(5)$$

But, distribution Co-efficient (Dmix) for mixed extraction is,

$$D_{mix} = \frac{[Ag(A).(S)]_{org} + [Ag(A).(H_2O)_n]_{org}}{[Ag]^+_{aq}} \dots\dots\dots(6)$$

Combining Eq. (2), (5) and Eq (6), we get

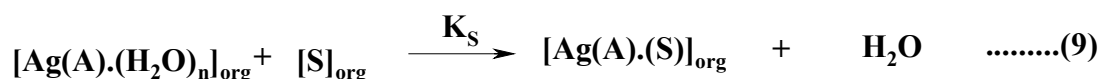
$$K = \frac{(D_{\text{mix}} - D_0)[H]_{\text{aq}}^+}{[HA]_{\text{org}} [S]_{\text{org}}} \dots\dots\dots(7)$$

Taking logarithm and rearranging,

$$\log K = \log (D_{\text{mix}} - D_0) - \log [HA]_{\text{org}} - \log [S]_{\text{org}} - \text{pH} \dots\dots\dots(8)$$

Extraction of Ag (I) with pure donor is negligible under the present condition.

The adduct formation reaction in the organic phase may be represented as



Degree of Synergism in Extraction and equilibrium constant:

The degree of synergism can be quantified by synergistic coefficient (SC). It is used to describe enhancement in the equilibrium distribution ratio when two or more extractants are used as a mixture for extraction.

$$S.C. = \log [D_{\text{mix}}/(D_0+D_s)] \dots\dots\dots (10)$$

Where D_{mix} , D_0 and D_s denote the distribution ratios of a metal ion with mixture of ligand and donor, pure ligand (O), and only donor (S) respectively. In the present case, $D_s = 0$

The apparent stability constant (β) is given by:

$$\beta = (D_{\text{mix}} - D_0) / D_0 [S] \dots\dots\dots(11)$$

Synergism was observed at all the compositions studied. Keeping the concentration of ligand constant it was observed that the synergistic coefficient increased with an increase in the concentration of the synergist donor in **Table: 2**, at fixed pH of the aqueous phase. Similarly, keeping neutral donor concentration constant, the synergistic coefficient increased with an increase in the ligand concentration in the organic phase at a given acid concentration Table: 3. The trend in S.C and β -value shown in Table: 2 and Table: 3, for neutral donors taken up here follow the order: TOPO > TBPO > TBP keeping parity with their electron donor abilities. Thus, TBP having much poor donor ability with respect to two phosphine oxides results only low values of stability constant in compare to TOPO and TBPO. Again If we compare the $\log K$ (ternary equilibrium constant) and $\log K_S$ (adduct formation

equilibrium constant) values Table: 4, it is observed that the above two parameters are found to be highest in case of tri-butyl phosphine oxide (TOPO). The $\log K_S$ values clearly show that TOPO is the most effective synergistic agent among the three organophosphorus donors used in present investigation. This trend can be correlated with the relative basic natures of the oxophosphorus donors. Somewhat similar trend was observed in the synergistic extraction of other transition metals and actinides²⁵⁻²⁶. Overall enhancement effects of neutral organophosphorus donor compounds are found to be very high. The liquid-liquid extraction of a metal ion with a chelating agent is essentially determined by the stability and extractability of uncharged metal complex e.g [Ag. (A). (S)] in present case.

Table: 2. Synergistic Extraction of Ag(I) with Fixed Concentration of 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone in Presence Different Concentration of Donor. [Ligand] = 0.35×10^{-3} (mol.dm⁻³), D₀ = 0.165, at pH = 3.0, Solvent = Cyclohexene.

Donor	Conc of donor (mol.dm ⁻³)	Dmix	(Dmix - Do)	(%) Extraction	S.C	logβ mol ¹
TOPO	0.0021	0.344	0.179	25.59	0.319	2.72
	0.0032	0.461	0.296	31.56	0.446	2.75
	0.0042	0.568	0.403	36.23	0.536	2.76
	0.0062	0.777	0.612	43.73	0.672	2.77
TBPO	0.0021	0.316	0.151	24.01	0.282	2.62
	0.0031	0.383	0.218	27.69	0.365	2.63
	0.0041	0.453	0.288	31.18	0.438	2.63
	0.0062	0.611	0.446	37.92	0.568	2.64
TBP	0.0054	0.306	0.141	23.44	0.268	2.19
	0.0069	0.347	0.182	25.76	0.323	2.20
	0.0084	0.396	0.231	28.36	0.381	2.22
	0.0109	0.456	0.291	31.32	0.441	2.20
	0.0165	0.643	0.478	39.14	0.591	2.24

Where, S.C = Synergistic co-efficient = $\log [D_{mix}/D_0]$

and β (mol¹) = $(D_{mix} - D_0) / D_0[S]$, apparent formation constant S = Donor

Table: 3. Synergistic Extraction of Ag(I) by Mixture of 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone and Donor From Aqueous Nitrate Medium at pH = 3.0 into Cyclohexene Solvent.

Donor (mol.dm ⁻³)	Ligand Conc. $\times 10^{-3}$ (mol.dm ⁻³)	Do	Dmix	[Dmix-Do]	% Extraction	S.C	logβ mol ¹
[TOPO] = 0.0021	0.35	0.165	0.344	0.179	25.59	0.319	2.72
	0.524	0.254	0.535	0.281	34.86	0.323	2.72
	0.750	0.381	0.798	0.417	44.38	0.321	2.72
	1.05	0.567	1.243	0.676	55.42	0.340	2.75
	1.40	0.796	1.751	0.955	63.64	0.342	2.76
[TBPO] = 0.0021	0.35	0.165	0.316	0.151	24.02	0.282	2.64
	0.524	0.254	0.492	0.238	32.98	0.287	2.65
	0.750	0.381	0.741	0.361	42.56	0.288	2.66
	1.05	0.567	1.138	0.571	53.23	0.299	2.68
	1.40	0.796	1.591	0.795	61.41	0.301	2.67
[TBP] = 0.0054	0.35	0.165	0.306	0.141	23.43	0.268	2.19
	0.524	0.254	0.474	0.221	32.26	0.270	2.20
	0.750	0.381	0.732	0.351	42.27	0.282	2.23
	1.05	0.567	1.101	0.534	52.41	0.287	2.24
	1.40	0.796	1.51	0.714	60.15	0.278	2.22

Table: 4. Values of the Binary (log k), Ternary (log K) Equilibrium Extraction Constants and Synergic Adduct Formation Constants (log K_s) for the Extraction of Ag(I) with 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone a and Mixture of Donor in Cyclohexene at T = 298 K.

Binary System		Ternary System		
Ligand	logk (Average)	Presence of Donor	logK (Average)	logK _s
2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone	-0.315	TOPO	2.45	2.77
		TBPO	2.31	2.63
		TBP	1.87	2.19

Table: 5. Comparison of Synergistic Constants for Ag (I) Extraction with some Synergist Extraction Systems from Nitrate Medium.

Synergic extraction system	Solvent	Log K _s (1*)	LogK _s (2*)
(HTTA) - (TBA ⁺)	Chloroform ¹⁷	-	10.9
(HIPT)- (TBA ⁺)	Chloroform ¹⁷	-	10.3
HTTA-TOPO	Chloroform ¹⁸	3.58	4.20
HTTA-TBP	Chloroform ¹⁸	2.15	
HTTA-Quinoline	Chloroform ¹⁸	5.56	
Caproic-Quilonine	Chloroform ¹⁸	4.56	
Caproic-TOPO	Chloroform ¹⁸	2.73	4.26
HA-TOPO	Cyclohexane	2.77	This work
HA- TBPO	Cyclohexane	2.63	□
HA-TBP	Cyclohexane	2.19	□

1* Stiochometry of Metal Complex is Ag: Ligand:Donor = 1:1:1

2* Stiochometry of Metal Complex is Ag: Ligand:Donor = 1:1:2

Table: 6. Thermodynamic Values for Extraction of Ag (I) from Aqueous Nitrate of Constant Ionic Strength with 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone and Mixture of Donor in Cyclohexene.

System	ΔH° (kJ .mol ⁻¹)	ΔS° (J K ⁻¹ .mol ⁻¹)	ΔG° (kJ.mol ⁻¹) at 27 ^o C
Ag(I) –Ligand	+ 4.738	+ 9.452	+ 1.903
Ag(I) –Ligand-TOPO	-19.732	-18.069	-14.324
Ag(I) –Ligand-TBPO	-21.664	-26.673	-13.524
Ag(I) –Ligand-TBP	-25.717	-48.553	-11.132

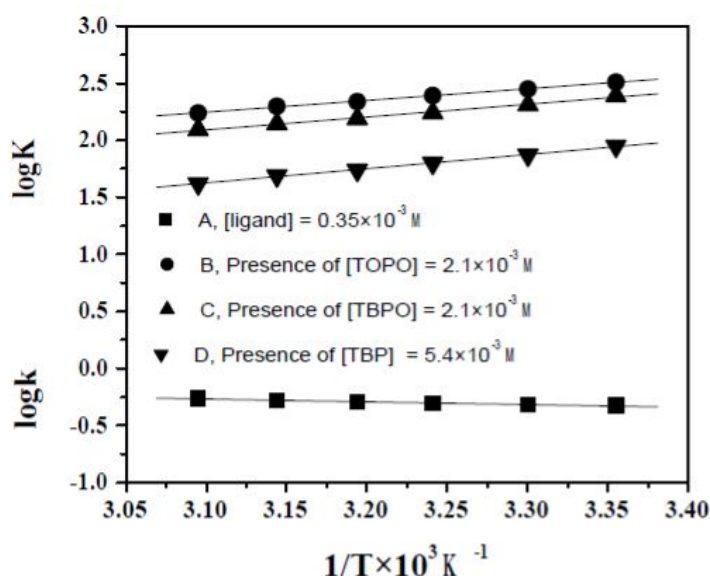


Figure- 6: Effect of temperature on the equilibrium extraction constant of Ag (I) at pH 3.0 of aqueous nitrate solution by fixed concentration of 2-hydroxy-1-naphthaldehyde thiosemicarbazone extractant dissolved in cyclohexene in absence and presence of donor. The line 'A' only presence of ligand, and 'B', 'C', 'D' lines are the synergistic mixture of different donor presence of fixed ligand concentration.

The adduct formation constant data of present Ag (I) with 2-hydroxy-1-naphthaldehyde thiosemicarbazone –donor systems were compared with corresponding data of other ligand-donor system [17-18] and value can be explained on the basis of acid dissociation constant (pKa) value of chelating ligand shown as in Table: 5. The tendency of orientation towards metal ion of the non-bonding electron pair of chelating ligand depends on its pKa value. When this orientation towards metal ion is less, then the residual positive charge over the metal ion is responsible for greater interaction with the incoming neutral donor. However quinoline forms a most stable adduct than does organophosphorus donor with silver chelates system, this seems to indicate that the stability order of chelate adducts depend on the donor sites of the chelates. The synergic constants for Ag (I) by the systems TTA-TBA⁺ and ITA –TBA⁺ exhibit larger values than the other tabulated values. In this case, the non-charged complexes Ag (ITA) and Ag(TTA), associated with the ion-pair of the reagents, TBA⁺-TTA⁻ and TBA⁺- ITA⁻ are transferred into the organic phase. The formation of the anionic complexes, Ag (TTA)₂⁻ and Ag(ITA)₂⁻, are extracted as the ion-pair with TBA⁺, and the adduct formation constants are high.

Extraction Mechanism and Thermodynamic Parameters:

The equilibrium extraction constants logk and logK for the studied complexes were obtained from the equilibrium metal concentration in the organic and aqueous phase using Eqs. 3 and 8. From the values of equilibrium extraction constant at the temperature range investigated, enthalpy changes were calculated using the Vant's Hoff equation²⁷.

$$\log K = -\Delta H^0/2.303RT + \Delta S^0/2.303RT$$

The plot of logK against 1/T in Figure- 6 is a straight line where the slope gives the enthalpy of reaction (ΔH^0) and intercept corresponds to entropy (ΔS^0) value and these data were used to obtain the corresponding free energy changes. The results are summarized in Table: 6. 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 resulting from two opposing processes: 1) the dehydration of the extracted cation and the hydration of the exchanged protons; 2) the metal coordination by the organic ligand and the deprotonation of the ligand²⁸. For ligands aggregated through hydrogen bonds, as typical for organophosphorus acids, this second process will also involve breaking hydrogen bonds. The dehydration of the metal cation generally involves a positive enthalpy variation ($\Delta H^0 > 0$) as a

result of the breakage of ion-water bonds, and a positive entropy variation ($\Delta S^0 > 0$) due to an increase of disorder in the system. The opposite will occur for the hydration of the proton. The less favorable enthalpy variation in the extraction of Ag (I) by TSN extractants, likely arises from the participation of the metal ion in larger chelate rings. In such complexes the hydrated sphere of Ag (I)-aqua complex is disrupted more extensively and the net entropy and enthalpy changes are positive. Such a pattern is typical of inner-sphere complexation²⁹. In adduct formation reaction the coordinates water molecule of Ag(I) extracted complex was release in addition of the such basic donor. The donor more basic than the H₂O molecule and forms stronger adduct bonds resulting in, the enthalpy being exothermic. Higher ΔH^0 for TOPO donor as compared to other two donor system suggests the higher degree of covalence in case of TOPO donor with Ag (I)- extracted as compared to other two donor likes TBPO and TBP. The ΔS^0 values were also calculated for three adduct systems in Table: 6. Hence, both the enthalpy and entropy changes favor the reaction, resulting in relatively large values of log K. Adduct formation reaction in the organic phase for synergistic chelates in three cases TOPO, TBPO and TBP mainly enthalpy stabilized with negligible entropy contribution. In case of TBP adduct system, lower ΔS^0 value in presence of donor may be due to the weaker interaction of the extractant molecules leading to the presence of more number of water molecules in the extracted species. The resultant ΔG^0 value was less negative for TBP while it was more negative for TOPO donor and incase of TBPO was moderate.

CONCLUSIONS

The extraction behavior of the Ag(I) from aqueous nitrate medium by 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone in cyclohexene at pH 3.0 in presence and absence of organophosphorus donor was studied using the following parameters:.

- 1) The first power dependence of the 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazone is observed, which forms Ag (A) as the extractable species is more favorable in the non-polar organic solvent.
- 2) In synergistic extraction, the first power dependence of the HA is observed. And presence of donor in extraction system one molecule of each donor is added to the synergistic extracted species in the cyclohexene solvent system. From the stoichiometry calculation, the adduct is formed in organic phase as [Ag (A).S] Among the three organophosphorus -donor, TOPO has shown a strongest synergistic effect due to having more basic character (K_H 8.9) than other two donors. The efficient synergist order as follows : TOPO>TBPO>TBP.

4) This experiment shows that the synergistic extraction is exothermic driven process. So with the increase of temperature extraction processes disfavorable. Whwere as binary extraction reverse order was found.

Such study of enhancement effects of organophosphorus donor on the chelating extraction of

Ag (I) in cyclohexene organic solvent is very encouraging and can be extrapolated in the field of hydrometallurgy.

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