



Efficiency of 2-dodecylaminopyridine for the liquid-liquid extraction of gold(III) from succinic acid medium

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Abstract

Extractive recovery of gold(III) from succinic acid solution with high molecular weight amine: 2-dodecylaminopyridine (2-DDAP) as a new extractant in xylene has been investigated. Extraction data indicates that 5×10^{-4} mol·L⁻¹ 2-DDAP is a very efficient and fast extractant. Gold(III) can be effectively extracted ($D = 414.16$) with 2-DDAP from 0.04 M succinic acid solution. The equilibrium of gold(III) from aqueous phase of succinic acid with 2-DDAP is achieved within 60 s. The extraction of gold(III) with 2-DDAP proceed at the interface according to ion pair formation mechanism. The best stripping solution from among the studied ones is the 4 M ammonia solution. The selective extraction of gold(III) from some precious and base metals was carried out by 2-DDAP using proposed method and the results obtained are found to be highly effective for synthetic sample.

1. Introduction

Precious metals possess specific chemical and physical properties; have paramount significance in industrial technology. The use of gold in many industrial applications has recently become extensive, e.g. biomedical area, catalysts, electronic and fuel cell devices [1-4]. However, concentration of gold in environment and geological materials are usually too low. Growing demand for gold makes it crucial and inevitable to recover the gold from increasing secondary sources. Thus, gold recovery is interesting due to its vast industrial applications, high market value and extensively used as precious metal, and the limited resource of this metal may explain the recent gold share value [5-7].

Several analytical methods have been reported for the separation and purification of gold such as precipitation [8,9], adsorption [10-13], membrane filtration technology [14,15], Solid phase extraction [16-18], and solvent extraction [19,20]. Solvent extraction of metals is already well established as efficient alternative to traditional techniques [21]. Different extractants have been developed and employed as extraction reagents for precious metals especially for gold (III) for both commercial and analytical purposes including tri-n-butylphosphate [22], cetylpyridinium bromide/tributyl phosphate [23], 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline [24], N-n-octylaniline [25], 1-octyl-3-methylimidazolium hexafluorophosphate [26], 4-(4'-methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol [27], N-methyl-N-butylhexylamide [28], furfuryl thioalcohol [29], 4-(4'-Fluorobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole [30]. However, some of solvent extraction system used large quantity of extractant in different organic solvent, which may cause some of the environmental and workers health problems. Furthermore,

most of the solvent extraction systems were conducted under the strong acidic condition [28,31-33] and resulted in severe corrosion to the equipment used for extraction purpose. For sustainability of the solvent extraction, it is necessary to find efficient, safer and greener solvent extraction system.

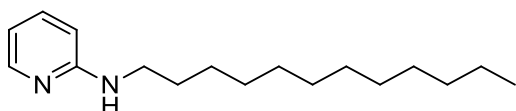
In this work, solvent extraction experiments have been performed to find out optimum conditions for efficient and selective extraction of gold(III) from aqueous phase of different organic acids. For this purpose, 2-dodecylaminopyridine (2-DDAP) as a new extractant was employed to evaluate the performance of gold(III) extraction from oxalic acid, malonic acid, succinic acid and citric acid solution. Various parameters such as solution pH, organic acid concentration, phase contact time, phase volume ratio (A/O) and diluents for organic phase preparation were investigated. The stripping of gold(III) from organic phase has been performed. The proposed method was also extended for the recovery of gold(III) from synthetic mixture of precious and base metals.

2. Experimental

2.1 Material and apparatus

A Shimadzu UV-Visible Spectrophotometer (UV 1800) with 1 cm² quartz cell was used for absorbance measurements and pH optimization was carried out by Elico digital pH meter Model LI -120 (± 0.01). All the chemicals used were of AnalaR grade and purchased from commercial suppliers Alfa Aesar (Thermo Fisher Scientific, Hyderabad, India) and Spectrochem (Spectrochem Pvt. Ltd., Mumbai, India). These are used as such without further purification. A stock solution

of gold (III) was prepared by dissolving 1 g HAuCl₄ in 250 mL of deionized water and standardized gravimetrically and other solutions were prepared by dissolving appropriate amount of H₂PtCl₆·6H₂O, PdCl₂, RuCl₃·3H₂O, RhCl₃·3H₂O, CuCl₂·2H₂O, NiCl₂·6H₂O and FeCl₃·6H₂O in deionized water. A series of working solutions were prepared by diluting the stock solution. An extractant, 2-dodecylaminopyridine was synthesized by reported method [34] and characterized by spectral techniques. Deionized water was invariably used throughout the experiments. The structure of extractant, 2-DDAP is shown as;



Scheme 1. Structure of extractant 2-DDAP.

2.2 Extraction experiment

To evaluate the extraction efficiency of 2-DDAP for gold(III) from its aqueous phase, xylene was used as the organic phase owing to its hydrophobic property and good solubility for extractant. An aqueous phase having 100 µg of gold(III), enough succinic acid and water were added to give 0.04 mol·L⁻¹ concentration with respect to succinic acid in total volume of 25 mL. The resulting aqueous phase and 10 mL organic phase of 5 × 10⁻⁴ mol·L⁻¹ 2-DDAP in xylene were mixed in separatory funnel and vigorously shaken at ambient temperature within appropriate time. After phase separation, gold (III) from organic phase was stripped with two 10 mL portions of 4 ammonia solution. The extract was evaporated to moist dryness and leached with 1 mL of dilute hydrochloric acid solution, and transferred in to 50 mL volumetric flask, 10 mL of 20% potassium iodide was added, the solution was mixed well and heated for 15 min in boiling waterbath. To the cooled solution, 10 mL of 10% stannous chloride solution was added and diluted upto the mark. The unstoppered flask was kept in boiling waterbath for 2 min. The solution was then cooled and the absorbance of reddish brown solution was measured at 400 nm against a reagent blank and gold was estimated by stannous chloride method [35]. The distribution ratio (D) was calculated as the ratio of gold(III) concentration in organic phase [Au]_{Org} to aqueous phase [Au]_{Aq} after extraction using equation,

$$D = \frac{[Au]_{Org}}{[Au]_{Aq}} \quad (1)$$

The percentage extraction (% E) of gold(III) was calculated by equation,

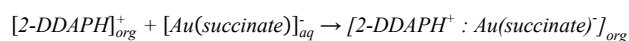
$$\% E = \frac{100 D}{D + \frac{V_{Aq}}{V_{Org}}} \quad (2)$$

Where V_{Aq} is volume of aqueous phase and V_{Org} is volume of organic phase.

2.3 Extraction mechanism

In the extraction experiments, extractant 2-DDAP shows very good extractability for gold(III), plausible extraction mechanism discussed here for understanding the nature of ion pair complex of gold(III) in succinic acid media with 2-DDAP. The mechanism of ion pair

complex was initiated through protonation of 2-DDAP to form cationic species, while anionic species was formed by combining succinic acid with gold(III) and both of these formed the ion pair complex as given [36].



The subscripts org and aq denote the species in organic and aqueous phases, respectively.

3. Results and discussion

3.1 Effect of aqueous phase pH on gold (III) extraction

Aqueous phase pH is one of the determining factors for gold(III) extraction by extractant [11,14]. To examine the behavior of the extractant for different pH values and to determine the optimum pH, we have performed the competitive extraction of gold(III) at different pH. The extraction properties of gold(III) by 2-DDAP were investigated over the pH range 1 to 10. Figure 1 shows the effect of aqueous phase pH on the extraction of gold(III) which clearly indicates that the quantifiable extraction was observed in the pH range 3 to 6 and this may due to stable ion pair formation of gold(III) with 2-DDAP [26,37], and efficacy of extraction decreased with rising pH of aqueous phase [38]. It seems that the basic medium is not favorable for extraction of gold(III) with 2-DDAP. Therefore the aqueous phase with pH 6 was used for further extraction experiments.

3.2 Effect of 2-DDAP molarity

The extraction behavior of gold(III) with various concentration of 2-DDAP in organic phase was studied. The 2-DDAP concentration was varied over the range 1 × 10⁻⁴ mol·L⁻¹ to 1 × 10⁻³ mol·L⁻¹. As shown in Figure 2, the increasing concentration of 2-DDAP shows positive effect on gold(III) extraction performance. In order to optimize the concentration of 2-DDAP required for maximum extraction, percent extraction values were plotted against concentrations and it observed that 99.40% extraction was found at 5 × 10⁻⁴ mol·L⁻¹. Therefore further extraction studies were carried out at this concentration.

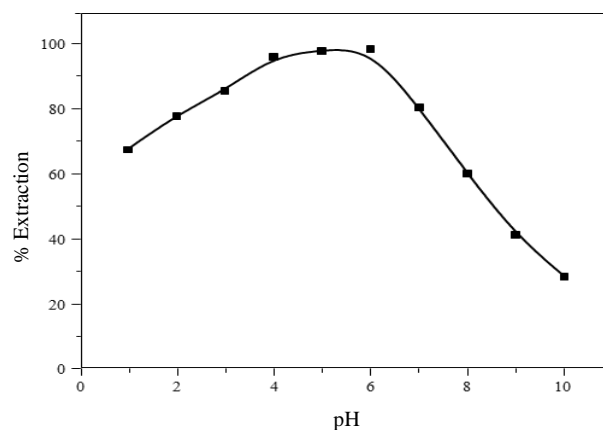


Figure 1. Effect of aqueous phase pH on gold(III) extraction. Experimental conditions: gold(III) = 100 µg, Succinic acid = 0.04 M, 2-DDAP = 5 × 10⁻⁴ mol·L⁻¹ in xylene, phase contact time = 60 s, strippant = 4 M ammonia.

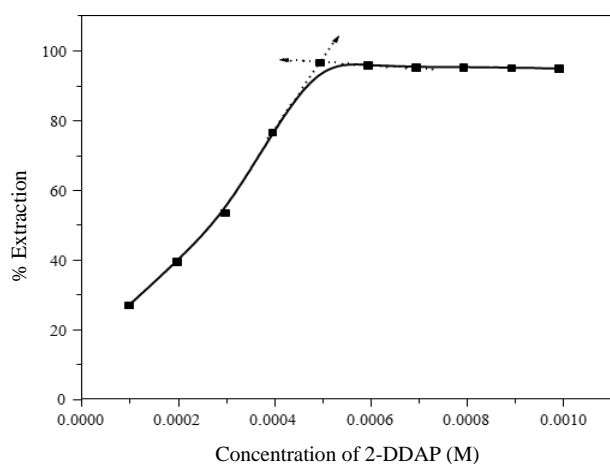


Figure 2. Effect of 2-DDAP molarity. Experimental conditions: gold(III) = 100 μg , Succinic acid = 0.04 M, pH = 6, Phase contact time = 60 s, stripping agent = 4 M ammonia.

3.3 Effect of organic acid salts concentration

It is well known that mineral acids present in aqueous phase played a key role in the solvent extraction process of gold. Some researchers have been developed the extraction of gold(III) from cyanide and hydrochloric acid solutions [14,15,23]. Now we have studied the extraction of gold(III) by 2-DDAP in presence of salts of malonic acid, oxalic acid, succinic acid and citric acid in aqueous phase, and varies in the concentration range 0.01 mol·L⁻¹ to 0.1 mol·L⁻¹, results obtained are presented in Figure 3. Obviously the extraction efficiency increased rapidly with increasing organic acids concentration in the range 0.01 mol·L⁻¹ to 0.04 mol·L⁻¹, then followed a gradual decline. The maximum extraction was found to be in the presence of succinic acid and it decreased from 99.40% to 61.80% by increasing concentration upto 0.1 mol·L⁻¹ in aqueous phase. This suggested that the addition of too much organic acid salt in aqueous phase reduces the probability of ion pair formation of gold(III) with 2-DDAP at interfacial region [39]. Maximum extraction showed by oxalic acid, malonic acid and citric acid is 89.80%, 95.60%, and 82.50%, respectively. In consideration of extraction efficiency, succinic acid exhibits as most excellent aqueous phase media for gold(III) extraction as compared to other acids [40]. It is evidence to that the ion pair exchange mechanism leads to high extraction efficiency by the use of succinic acid in aqueous phase for extraction of gold(III) by proposed method. Finally, neither third phase formation nor stable emulsion was observed in this series of solvent extraction experiments. Therefore, for further studies of gold(III) extraction, an aqueous phase containing 0.04 mol·L⁻¹ succinic acid was used.

3.4 Effect of diluents as organic phase

Generally, solvent extraction of precious metals is dependent on the nature of diluents used during extraction experiments; therefore, selection of proper diluent for organic phase preparation is important for extraction. A number of diluents were tested for the extraction of gold(III) in order to assess a suitable solvent for extraction of ion pair complex of gold(III) with 2-DDAP. The results obtained by the use

of different diluents are presented in Table 1. It is found that extraction of gold(III) from 0.04 mol·L⁻¹ succinic acid media was achieved, if 2-DDAP solution was prepared in xylene, toluene and ethylbenzene respectively, while extraction was found incomplete in other diluents. The results showed no linear relation between dielectric constant and polarity of diluents and the extraction [41]. The use of xylene as solvent resulted in higher percentage extraction of gold(III) even though the dielectric constant of xylene is not so high, hence recommended for further experiments.

3.5 Effect of phase contact time

The extraction behavior of gold(III) was investigated at varied contact times of aqueous and organic phase from 20 s to 180 s. Figure 4, shows that the extraction of gold(III) reached maximum within 60 s, and after that the extraction remained almost constant without significant changes. The results indicate that 2-DDAP enables fast extraction of gold(III) as compared with previously employed extractants. In consideration of sufficient extraction time, 60 s was chosen as contact time for selective extraction experiments of gold(III).

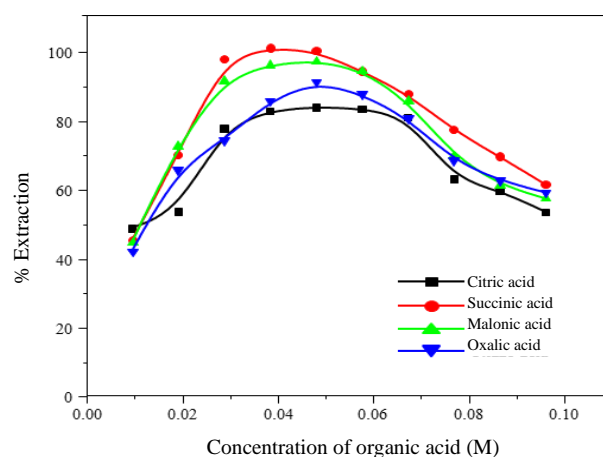


Figure 3. Effect of organic acid salts concentration. Experimental conditions: gold(III) = 100 μg , pH = 6, 2-DDAP = 5×10^{-4} mol·L⁻¹ in xylene, Phase contact time = 60 s, strippant = 4 M ammonia.

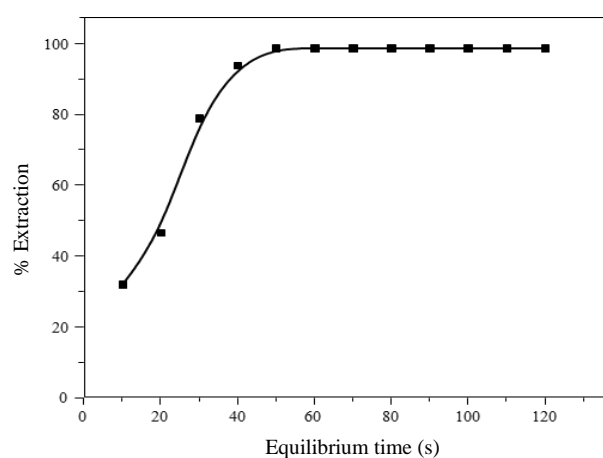


Figure 4. Effect of phase contact time. Experimental conditions: gold(III) = 100 μg , Succinic acid = 0.04 M, pH = 6, 2-DDAP = 5×10^{-4} mol·L⁻¹ in xylene, strippant = 4 M ammonia.

Table 1. Effect of diluents on percentage extraction and distribution ratio of gold (III).

Diluent	Dielectric constant	Dipole moment	Density	%E	D
Xylene	2.20	0.07	0.861	99.40	414.16
Toluene	2.38	0.31	0.867	95.15	44.04
Benzene	2.28	-	0.879	89.60	21.85
Anisole	4.33	1.38	0.990	E	E
Chloroform	4.81	1.15	1.489	51.12	2.62
n-Butanol	17.51	1.66	0.81	41	1.73
Dichloromethane	8.93	1.14	1.326	77.80	8.84
Ethylbenzene	2.41	-	0.867	92.70	31.74
n-Hexene	1.88	0.08	0.650	61.20	3.94

E = Emulsion

3.6 Effect of A/O phase volume ratios

The A/O (aqueous phase: organic phase) volume ratio also has remarkable influence on the solvent extraction process of precious metals. Several workers have reported A/O phase volume ratio was 1 for extraction of gold(III) [14,15,20]. To evaluate the extraction potential of 2-DDAP towards gold (III) under proposed conditions, the effect of phase ratio was investigated covering different A/O phase volume ratios from 1:1 to 10:1. The extraction of gold(III) was maximum when volume ratio of aqueous phase to organic phase from 1:1 to 5:1, when the ratios were higher than 5:1, the extraction efficiency had decreased. Notably, 2-DDAP is a best extractant, and shows manifold distribution ratio for gold(III), $D = 414.16$ than reported extraction system. Considering the higher distribution ratio and extraction efficiency, the A/O phase volume ratio 2.5 was used throughout this study.

3.7 Stripping studies

After moving the gold(III) from aqueous phase to organic phase, a stripping step was performed with two 10 mL portions of stripping

reagents for removing the gold(III) existing in the organic phase to aqueous phase for recovery. In the present work, various reagents such as sodium hydroxide, potassium hydroxide, sodium chloride, ammonia and thiourea were tried for back extraction of gold(III) from loaded organic phase. Solution of ammonia is found to be effective agent for gold(III) stripping, whereas other reagents show poor stripping performance. The results obtained are presented in Table 2.

3.8 Effect of foreign ions

The extraction of 100 μg of gold(III) with the proposed method was investigated in the presence of foreign ions. Initially the foreign ions were added to the gold(III) solution in large excess. When interference was intensive, the tests were repeated with successively smaller amounts of foreign ion. The tolerance limit was set at the amount of the foreign ion that could be present to give an error less than $\pm 2\%$ in the extractive recovery of gold(III). The results of these experiments are presented in Table 3. It was observed that the method is free from interference from a large number of ions. The reproducibility of gold(III) extraction was investigated from six replicate measurements.

Table 2. Percentage stripping of gold (III) with different stripping reagents.

Entry	Stripping reagent	% Stripping
1	NaOH (1-4 M)	12.40
2	KOH (1-4 M)	10.76
3	NaCl (1-4%)	22.47
4	NH ₃ (4 M)	100
5	Thiourea (1-4 M)	37.80

Table 3. Effect of foreign ions.

Foreign ions	Tolerance limit (mg)	Foreign ion	Tolerance limit (mg)
Rh(III)	2.0	Cu(II)	20.0
Pd(II)	1.0	Zn(II)	30.0
Ru(III)	1.0	Hg(II)	15.0
Pt(IV)	2.0	Mg(II)	25.0
Cr(III)	30.0	Sn(II)	15.0
Mn(II)	25.0	Sr(II)	10.0
Fe(III)	30.0	Pb(II)	15.0
Fe(II)	30.0	Ti(IV)	20.0
Co(II)	30.0	U(VI)	10.0
Ni(II)	35.0	Bi(III)	15.0

4. Selective extraction of gold(III)

4.1 Separation of gold(III) from binary mixture of base metals

The determination of small amounts of gold(III) in minerals containing base metals is difficult, hence it was decided to evaluate the potential of 2-DDAP as an extractant for gold(III) from synthetic solutions of base metals. The proposed method allowed for selective separation and determination of gold(III) from binary mixture containing Fe(III), Co(II), Ni(II) and Cu(II). This method permits the separation of gold(III) from commonly associated base metals due to their differences in extraction conditions. Gold(III) was successively separated from binary mixture of Fe(III), Co(II), Ni(II) and Cu(II) by its extraction with 5×10^{-4} mol·L⁻¹ 2-DDAP in xylene at pH 6 from 0.04 mol·L⁻¹ succinic acid within 60 s. Under this condition Fe(III), Co(II), Ni(II) and Cu(II) remain quantitatively in aqueous phase and determined by spectrophotometrically [42]. The extracted gold(III) into organic phase from the mixture of studied metals was stripped with two 10 mL portion of ammonia. The extract was evaporated to moist dryness and leached with 1 mL dilute hydrochloric acid solution and determined by spectrophotometrically by stannous chloride method. Recovery

of gold(III) from studied base metals was found to be efficient and results of experiments are presented in Table 4.

4.2 Separation of gold(III) from multicomponent synthetic mixture

Natural occurrence of gold is always associated with precious and base metals; hence its selective separation from these metals is of great importance. The selectivity shown for gold(III) by 2-DDAP is obviously determinant key point that requires evaluation. Therefore again focusing the research on the use of succinic acid in aqueous phase solution with more practical interest, aqueous phase of gold(III) with Ru(III), Rh(III), Pd(II), Pt(IV) and studied base metals, the extraction experiments were performed by proposed method. There is a possibility of extraction of Ru(III), Rh(III), Pd(II) and Pt(IV) but these co-extracted metal ions cannot get stripped by ammonia solution. The overall results obtained are illustrated in Table 5. The displayed extraction values are depicted significant digits, in order to allow the correct quantification. As expected, there are no significant differences between feed amount and extracted amount of gold(III). Therefore it can be presumed that 2-DDAP is selective for gold(III) in the presence of precious and base metals.

Table 4. Separation of gold (III) from binary mixture of base metals.

Composition of metals (µg)	Recovery of Au(III) (%)	R.S.D.	*Recovery of added metals (%)	R.S.D.
Au(III) 100, Fe(III) 500	99.40	0.19	99.60	0.19
Au(III) 100, Co(II) 500	99.38	0.25	99.50	0.16
Au(III) 100, Ni(II) 500	99.50	0.17	99.60	0.13
Au(III) 100, Cu(II) 500	99.40	0.15	99.70	0.07

R.S.D: relative standard deviation, *: Average six determinations

Table 5. Selective extraction of gold (III) from synthetic mixture.

Composition (µg)	Gold found (µg)	R.S.D
Au 100, Ru 500	99.40	0.02
Au 100, Rh 500	99.40	0.4
Au 100, Rd 500	99.36	0.3
Au 100, Pt 500	99.20	0.2
Au 100, Ru 500, Rh 500	99.50	0.5
Au 100, Ru 500, Pd 500	99.30	0.3
Au 100, Ru 500, Rh 500,	99.44	0.4
Au 100, Ru 500, Rh 500, Pd 500	99.30	0.1
Au 100, Ru 500, Rh 500, Pt 500	99.30	0.2
Au 100, Ru 500, Pd 500, Ru 500, Pt 500,	99.10	0.5
Fe 500, Co 500, Ni 500, Cu 500		

5. Conclusions

This systematic experimental study of the extraction of gold(III) by 2-DDAP from succinic acid media shows that it is an effective system for the recovery of gold(III) from precious and base metals. The present investigation highlights that 2-DDAP is very active ion-pair forming reagent which is highly basic than reported amines as extractants for extraction of gold(III). Extraction of gold(III) does not need the addition of any modifier and extracted in single step from organic acid solution at pH 6. The stripping reagents used

are simple and convenient for selectivity and separation of gold(III). The proposed method showed a remarkable high affinity and selectivity towards gold(III) under the optimized conditions and expected to be the new benchmark for the separation of gold(III) from precious metals.

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