SIMULTANEOUS SOLVENT EXTRACTION OF METAL IONS WITH THIACROWN ETHERS STUDIED USING INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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Abstract

Simultaneous solvent extraction of ten metal ions (Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}) with three thiacrown ethers, namely 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) in 1,2-dichloroethane was studied using inductively coupled plasma-mass spectrometry (ICP-MS). Picric acid was used as counter ion. Key extraction parameters such as contact time, pH, ligand and counter ion concentrations were investigated. The three thiacrown ethers show high selectivity towards Ag^{+}, followed by Hg^{2+} and Cu^{2+} over the other metal ions studied. Under the optimized conditions, 10 ppm Ag^{2+} was selectively extracted from 1×10^{-3} M picric acid at pH 5 for 12S4, pH 4 for 15S5 and 18S6 into 1,2-dichloroethane containing 2×10^{-4} M ligand. This procedure was applicable to the selective extraction and determination of Ag^{+} from river water sample. The stoichiometries of the extracted complex is also established.

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Introduction

Solvent extraction, in conjunction with suitable ligands, has been widely used for the pre-concentration and separation of metal ions. Among the various ligands useful for metal ion complexation are the crown ethers and their analogues[1]. Crown ethers have been extensively investigated and are known to be effective for the extraction of hard and soft metal ions with the assistance of an appropriate counter anion[2]. Thiacrown ethers are a class of crown ethers where the donor oxygen atoms on the macrocyclic ring are partially or totally replaced by sulphur atoms. Thiacrown ethers are classified as a soft Lewis bases and are well-known to interact selectively with soft Lewis acids.

Accordingly, most of the past research efforts has focused on thiacrown ether complexation with soft or borderline metal ions[3], such as Cu^+, Cu^{2+}, Ag^+ and Hg^{2+} [4,5]. Several excellent review articles dealing with the coordination chemistry of 12 to 16-membered thiacrown ethers have been published[6,7]. Sevdic *et al.*[4,5] studied the complex formation properties of thiacrown ethers containing four, six and eight sulphur donor atoms with Ag^+ and Hg^{2+}, picrate and perchlorate serving as counter ions. Complexes of the ratio (metal : ligand) 1 : 1 and 2 : 1 for Hg^{2+} and 1 : 1, 2 : 1 and 3 : 1 for Ag^+ with six sulphur ligand, 1 : 1 for Hg^{2+} and 1 : 1 and 2 : 1 for Ag^+ with four sulphur ligand had also been reported. Ring size effect on the structure of the crown complex has also been discussed. It is further noted that Ag^+ form the most stable complexes with the six-membered sulphur ligand over the eight and four ones. Solid state complexes of Ni^{2+}, Co^{2+} and third state metal ions such as Cr^{3+}, Co^{3+} and Fe^{3+} with thiacrown ethers (9S3, 10S3, 12S3, 18S6, 24S6) were also reported[8-12]. Due to their excellent selectivity, they readily lend themselves as useful analytical reagents for the determination of Hg^{2+}, Ag^+ and Cu^{2+} [3, 13-14]. Accordingly, extraction of these metal ions with thiacrown ethers have been studied much more widely than extraction with other types of crown ethers[15-17]. Saito *et al.*[3,18], extensively studied the extraction behaviour of Cu^{2+} with 12 to 16-membered tetrathiacrown ether using tetraphenylborate (TPB) or picrate (Pic) as counter ions. The use of a few thiaethers as chemical sensors have also been reported[19,20].

Since the introduction of the first commercial instrument in 1983[21], inductively coupled plasma-mass spectrometry (ICP-MS) has gained prominence as a powerful technique for elemental analysis. ICP-MS offers rapid and simultaneous multi-element analysis, with detection limits ranging from parts per billion to parts per trillion. Other unique capabilities of ICP-MS include, relatively simple spectra and the ability to conduct isotopic analysis[22,23]. ICP-MS has currently become a universally accepted analytical technique for multi-element determination in diverse fields such as environmental[24], geological[25,26], industrial[27], biological and clinical[28,29].

It should be pointed out that, in all previous reports on the extraction using thiacrown ethers, only one metal ion was studied at a time. In the present work, however, the ICP-MS is applied for the determination of several metal ions (Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}) after their simultaneous solvent extraction with three cyclic thiacrown ethers namely 1,4,7,10-tetrathiacyclododecane **(12S4)**, 1,4,7,10,13-pentathiacyclopentadecane **(15S5)** and 1,4,7,10,13,16-hexathiacylooctadecane **(18S6)** **(Figure 1)**. Picric acid was used as counter anion. Factors that contribute to the extraction in the studied system such as contact time, the concentration of H^{+}, ligand and counter ion concentrations and selectivity amongst the metal ions are investigated.

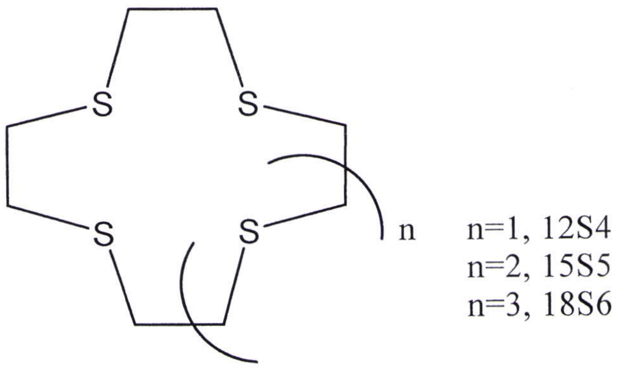

Fig. 1. Chemical structure of thiacrown ethers studied

Experimental

Apparatus

A Perkin Elmer Elan 6100 inductively coupled plasma-mass spectrometry (ICP-MS) with version 2.0 software was used in the studies. The instrument conditions and general method parameters are listed in **Table 1**. An Orion Ion Analyzer model EA940 was used for pH measurements. A mechanical shaker (Stuart Scientific, UK) was used for extraction. De-ionized water was produced from Millipore Milli-Q plus.

Table 1: ICP-MS instrumental operating conditions and data acquisition parameters

Condition / parameters	Result
ICP parameters	
R.f. power (W)	1000
Coolant argon flow rate (L min^{-1})	15
Auxiliary argon flow rate (L min^{-1})	1
Nebulizer argon flow rate (L min^{-1})	97
Operating frequency (MHz)	40
Sample introduction system	Cross flow nebulizer
Sample cone	Nickel with a 1.1 mm orifice
Skimmer cone	Nickel with a 0.9 mm orifice
Scanning mode	Peak hopping
Pressure (quadrupole analyzer) ICP (Torr)	$4.18 \text{ X } 10^{-5}$
Number of replicate	2

Chemical and Reagents

Stock solution (100 ppm) containing mixture of metals (sulfates of Zn^{2+}, Cd^{2+}, V^{4+}, Ni^{2+}, Cu^{2+}, Mn^{2+}; nitrates of Mg^{2+}, Co^{2+}, Ag^{+} and chloride of Hg^{2+} in a final volume of 250 mL were prepared by dissolving appropriate amount of metal salt in 2% HNO_3 solution.

Thiacrown ethers, 12S4, 15S5 and 18S6 (Aldrich) were used without further purification. Appropriate amount (0.01 M) of the thiacrown ether were dissolved in 1,2-dichloroethane (Merck).

A standard solution (0.01 M) of picric acid (BDH) was prepared by dissolving 0.229 g of the dried acid in 100 mL of de-ionized water. A 1 M sodium acetate (Riedel-deHaen) solution was prepared by dissolving 34.02 g of the salt in 250 mL de-ionized water.

For the determination of Ag^+ in real sample, river water was collected from Waterfall River, Penang, Malaysia. The water was filtered to remove suspended particles.

Liquid-Liquid Extraction

An aliquot sample solution (5 mL) containing a mixture of metal ions (10 ppm each) and picric acid (1×10^{-3} M) was placed in 100 mL stoppered conical flask. The pH was adjusted to the desired value with sodium acetate (1 M). An organic solution (5 mL) containing

2×10^{-4} M thiacrown ether in 1,2-dichloroethane was added. The mixture was shaken mechanically for 45 min at room temperature. After shaking, the phases were allowed to settle, separate and metal ions concentration left in the aqueous phase was determined using ICP-MS. The amount of the metal ion extracted into the organic phase was determined by difference.

Distribution Equilibrium of Metal Ion

The distribution equilibrium of metal ion (M^{n+}) from an aqueous picrate (Pic^-) medium with thiacrown ether (L) in the present system can be described in general according to *Eq*. (**1**). The extraction constant, K_{ex} is defined by *Eq*. (**2**).

$M^{n+} \quad + \quad mPic^{-} \quad + \quad n(L)_{org} \rightleftharpoons [MPic_{m}(L)_{n}]_{org}$ - - - - - - - **(1)**

$K_{ex} = [MPic_{m}(L)_{n}]_{org} / [M^{n+}][Pic^{-}]^{m}[L]^{n}_{org}$ - **(2)**

The distribution ratio (D) can be calculated as in *Eq.* (**3**).

$D = [M^{n+}]_{org} \; / \; [M^{n+}] \; = K_{ex}[Pic^{-}]^{m}[L]^{n}_{org}$ - **(3)**

Where $D = [MPic_{m}(L)_{n}]_{org} / [M^{n+}]$

$\mathrm{Log}D = \mathrm{Log}\,K_{ex} \; + \; m\,\mathrm{Log}[Pic^{-}] \; + \; n\,\mathrm{Log}[L]_{org}$ - **(4)**

In the presence of two species (M_1Pic_m) and (M_2Pic_m) in the aqueous phase (where M_1 and M_2 refer to different species of metal ions), then the distribution ratio can be written as

$D \; = \; [MPic_{m}L_{n}]_{org} \; / \; [M_1Pic_{m}] \; + \; [M_2Pic_{m}]$ - **(5)**

The selectivity (β) among the species can be related to the relative extraction constant K_{ex1} and K_{ex2} is given by *Eq.* **6** [30].

$\beta \; = \; K_{ex2} \; / \; K_{ex1} \; = \; D_2 \; / \; D_1$ - **(6)**

Results and Discussion

Effect of Contact Time

The solution was shaken on a mechanical shaker from 5 to 45 min. Results show that all the thiacrown ethers undergo a maximum extraction for Ag^+ (**Fig. 2**) after shaking for 10 min or longer, followed by Hg^{2+} and Cu^{2+}. However, once the maximum extraction has reached, increasing of contact time has no significant effect on the extraction. Therefore, an equilibrium time of 45 min was adopted for subsequent extraction studies to ensure complete extraction. This period of time was also found to be the best by Ikeda and Abe[31] on their solvent extraction of Cu^{2+} with tetrathiacrown ether derivative.

Effect of pH

The effect of pH on the metal extraction by the three ligands is summarized in **Figure 3**. The degree of extraction is found to increase with pH for Ag^+, Hg^{2+} and Cu^{2+} when 12S4 is used as extractant. A similar trend in pH extraction profile is exhibited for Hg^{2+} and Cu^{2+} when 15S5 and 18S6 are used as extractants, reflecting that the thiacrown ether's extraction efficiency for Hg^{2+} and Cu^{2+} are highly dependant on the ionization of picric acid in the medium. Therefore, pH 5 is the optimum pH for the extraction of Hg^{2+} and Cu^{2+} with 12S4, and pH 4 is the best for 15S5 and 18S6 systems. The percentage of extraction slightly decreases at pH lower or higher than the optimum pH for the extraction of Hg^{2+} and Cu^{2+} in all the studied systems. This pH profile agree well with the findings of Saito *et al.*[18] on their solvent extraction of Cu^{2+} with 12S4 but do not agree well with the findings of Ikeda and Abe[31], were Cu^{2+} can be extracted quantitatively (100 %E) at pH above 6 when extracted with 12S4 derivative.

No noticeable effect of pH on the extraction of Ag^+ with 15S5 and 18S6 was observed. A little acceptance at the acidic medium (pH 2) on the extraction of Ag^+ with 12S4 was observed (**Fig 2A**). However, increasing the pH of the aqueous solution enhances the formation of the complex, which reaches a maximum at pH ~ 4. These findings are a reflection of the independence of Ag^+ on the ionization of the counter anion on its complexation with 12S4. Therefore, pH 5 for 12S4 and pH 4 for 15S5 and 18S6 are used in subsequent work.

The %E values for the other metal ions, (Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) are below 8% (Log D < -1) for both 12S4 and 15S5 and slightly more than 15% (Log D < -0.8) for 18S6. This implies that these metal ions were very poor extracted under the studied conditions. Therefore, due to the favourable extraction characteristics of these ligands towards Ag^+, Hg^{2+} and Cu^{2+}, no further experiments are carried out involving the other metal ions.

Effect of Ligand Concentration

The influence of 12S4, 15S5 and 18S6 concentration was studied by extracting the metal ions with different amount of ligands, varied from 2×10^{-5} to 6×10^{-4} M. The extraction was carried out at the respective optimum pH (5 for 12S4 and 4 for both 15S5 and 18S6). Overall results show that the extraction was optimum when the ligand concentration $\geq 2 \times 10^{-4}$ M. **Figure 4** shows the effect of 12S4, 15S5 and 18S6 concentration on the distribution ratio (Log D) for Ag^+, Hg^{2+} and Cu^{2+} using 1×10^{-3} M picrate concentration. A good linear dependence on ligand concentration with a normal slopes of 0.5 for Ag^+ and Hg^{2+}, 2 for Cu^{2+} with 12S4, 1.5 for Ag^+, 2 for Hg^{2+}, 1.4 for Cu^{2+} with 15S5 and 1.5 for Ag^+, 0.4 for Hg^{2+} and 1.0 for Cu^{2+} with 18S6. This dependence confirms the general applicability of Eq. 3 in describing the extraction process. These results indicated that ligand 12S4 form complexes of ratios of 1:2 with Ag^+ and Hg^{2+} and 2:1 with

Cu^{2+}, ligand 15S5 form complexes of ratios of 3:2 with Ag^{+} and Cu^{2+} and 2:1 with Hg^{2+}, and ligand 18S6 form complexes of ratios of 3:2 with Ag^{+}, 1:2 with Hg^{2+} and 1:1 with Cu^{2+} in the presence of picrate anion. Therefore, 2×10^{-4} M of thiacrown ethers was adopted as a suitable concentration for subsequent extraction study.

Effect of Picrate Concentration

A study of picrate ion concentration varied from 5×10^{-5} to 1.4×10^{-3} M was examined under constant ligand concentration (2×10^{-4} M) and pH 5 for 12S4 and pH 4 for both 15S5 and 18S6. **Figure 5** shows the effect of picrate concentration on the distribution ratios of Ag^{+}, Hg^{2+} and Cu^{2+}. The log D values linearly increase with increase in the picrate concentration for all cases. The slopes of the logarithmic plot of D vs. picrate concentration were found equal to 0.5 for Ag^{+}, 0.4 Hg^{2+} and 1 for Cu^{2+} with 12S4, 0.7 for Ag^{+}, 0.2 for Hg^{2+} and 0.5 for Cu^{2+} with 15S5 and 1.5 for Ag^{+}, 0.4 for Hg^{2+} and 0.6 for Cu^{2+} with 18S6. These results indicate that two mole picrate is associated with Ag^{+} and Hg^{2+} ions while one moles for Cu^{2+} when extracted with 12S4 from picrate medium. However, 0.7 moles of picrate are needed for the extraction of one mole Ag^{+} with both 15S5 and 1.5 for 18S6 ligands, while 0.5 mole of picrate is necessary for the extraction of Cu^{2+} with 15S5 and 0.4 mole of picrate is needed for the extraction of Hg^{2+} with 18S6.

Separation

Under the optimum extraction system of 2×10^{-4} M ligand and 1×10^{-3} M picrate as a counter anion, the percentage extraction (%E) of the studied metal ions with 12S4, 15S5 and 18S6 is in the order $Ag^{+} >> Hg^{2+} > Cu^{2+}$, $Ag^{+} >> Cu^{2+} > Hg^{2+}$ and $Ag^{+} >> Hg^{2+} > Cu^{2+}$ respectively. The separation factor of metal ions are summarized in Table 2. The table shows that all the thiacrown ethers are very selective towards Ag^{+}.

Table 2: Separation factor (β) of metal ions by different ligands

Metal	β		
	12S4	15S5	18S6
Ag / Hg	16.93	8.32×10^3	256.88
Ag / Cu	1.78×10^3	135.32	460.96
Hg / Ag	5.90×10^{-2}	1.20×10^{-4}	3.89×10^{-3}
Hg / Cu	105.26	1.60×10^{-2}	1.79
Cu / Ag	5.61×10^{-4}	7.39×10^{-3}	2.17×10^{-3}
Cu / Hg	9.50×10^{-3}	16.48	0.56

These results further show that 15S5 is the best ligand for the extraction and separation of Ag^+ or Cu^{2+} in the presence of Hg^{2+} ($\beta = 8.32 \times 10^3$ and 16.48 respectively), while 12S4 was found to be the best ligand for a selective separation of Ag^+ or Hg^{2+} in the presence of Cu^{2+} ($\beta = 1.78 \times 10^3$ and 105.26 respectively). Poor selectivity of 18S6 among Hg^{2+} and Cu^{2+} have also been observed.

Determination of Ag^+ in river water sample

The determination of Ag^+ in a river water sample was conducted using the proposed extraction procedure. Firstly, the water was directly analyzed with ICP-MS to determine the metal ions content. The main metal ions found in the river water are Mg^{2+} (194 ppb), Zn^{2+} (3 ppb), Mn^{2+} (2 ppb) and Ca^{2+} (2001 ppb), but Ag^+ was not detected in the sample. The data are average of three determinations mainly carried out from different spots. Next, various concentration of Ag^+ (5, 10, 20, 40 ppm) was spiked respectively to the samples. The extraction results of these spiked samples are summarized in Table 3.

Overall results proved that all of the three thiacrown ethers show significant extraction (> 90%) of Ag^+ in the river water sample. Up to 10 ppm of Ag^+ was extracted quantitatively (100% E) by 15S5 and 18S6. However, the percentage of extraction slightly decreased when the spiked Ag^+ level was increased.

Table 3: %E of Ag^+ from spiked river water sample

Ag^+ spiked (ppm)	%E		
	12S5	15S5	18S6
5	95.8 (0.5)	100 (0.1)	100 (0.1)
10	93.8 (0.8)	100 (0.1)	100 (0.1)
20	91.4 (0.3)	98.0 (0.3)	98.7 (0.3)
40	90.2 (0.6)	97.7 (0.5)	97.8 (0.9)

* n = 3

Conclusion

A simultaneous solvent extraction system having excellent selectivity towards Ag^+ has been developed using the thiacrown ethers (12S4, 15S5 and 18S6) as macrocyclic neutral ligands and picrate as counter anion. The selectivity trend of these ligands are found to be the best for Ag^+, followed by Hg^{2+} and Cu^{2+}. However, negligible extraction was observed for other studied metal ions. On the whole, the results obtained are in agreement with those obtained by single-element analysis but we believe the present approach give more realistic information about the selectivity behaviour of these kind of macrocyclic ligands towards metal ions in a mixture. This extraction-ICP-MS method was successfully applied for the separation of Ag^+ in river water sample. The immobilization of these ligands for analytical applications under batch and flow conditions are actively being persued in our laboratories.

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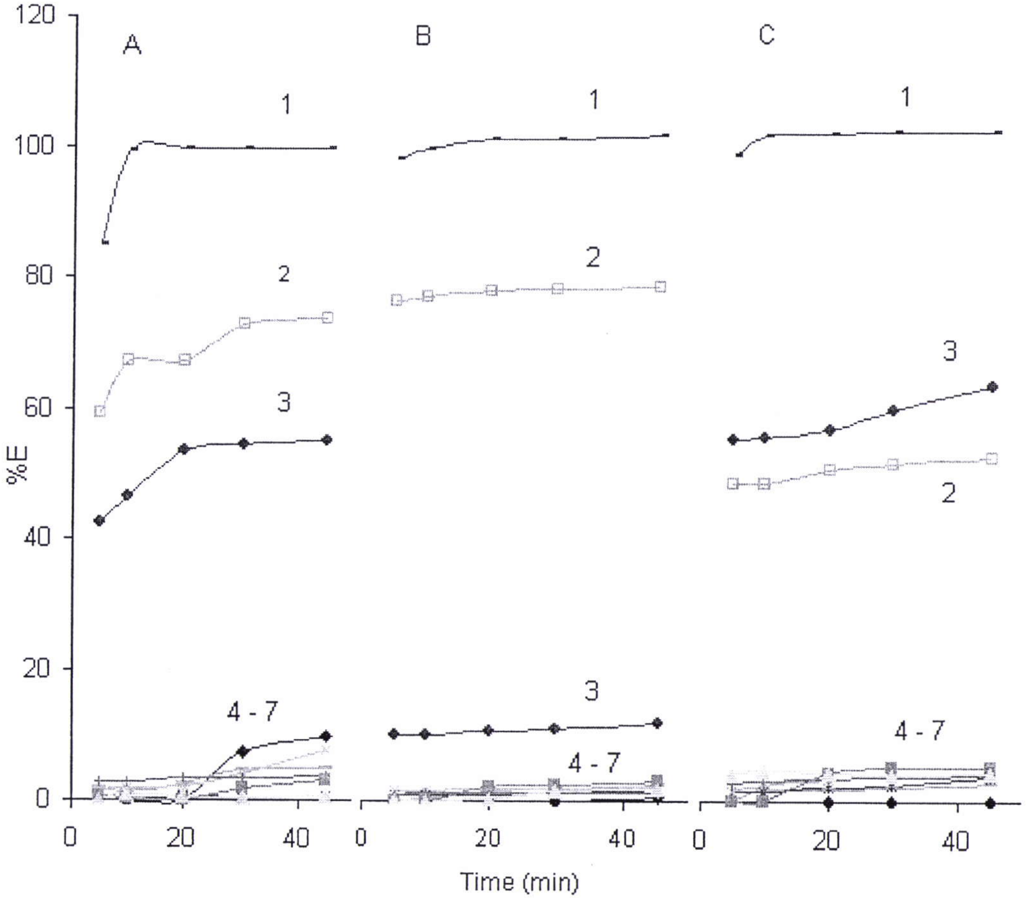

Fig.2. Effect of equilibrium time on the extraction of metal ions (1= Ag^+, 2= Hg^{2+}, 3= Cu^{2+}, 4-7= Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) with 2×10^{-4} M thiacrown ether (A= 12S4, B= 15S5, C= 18S6). Picrate concentration 1×10^{-3} M.

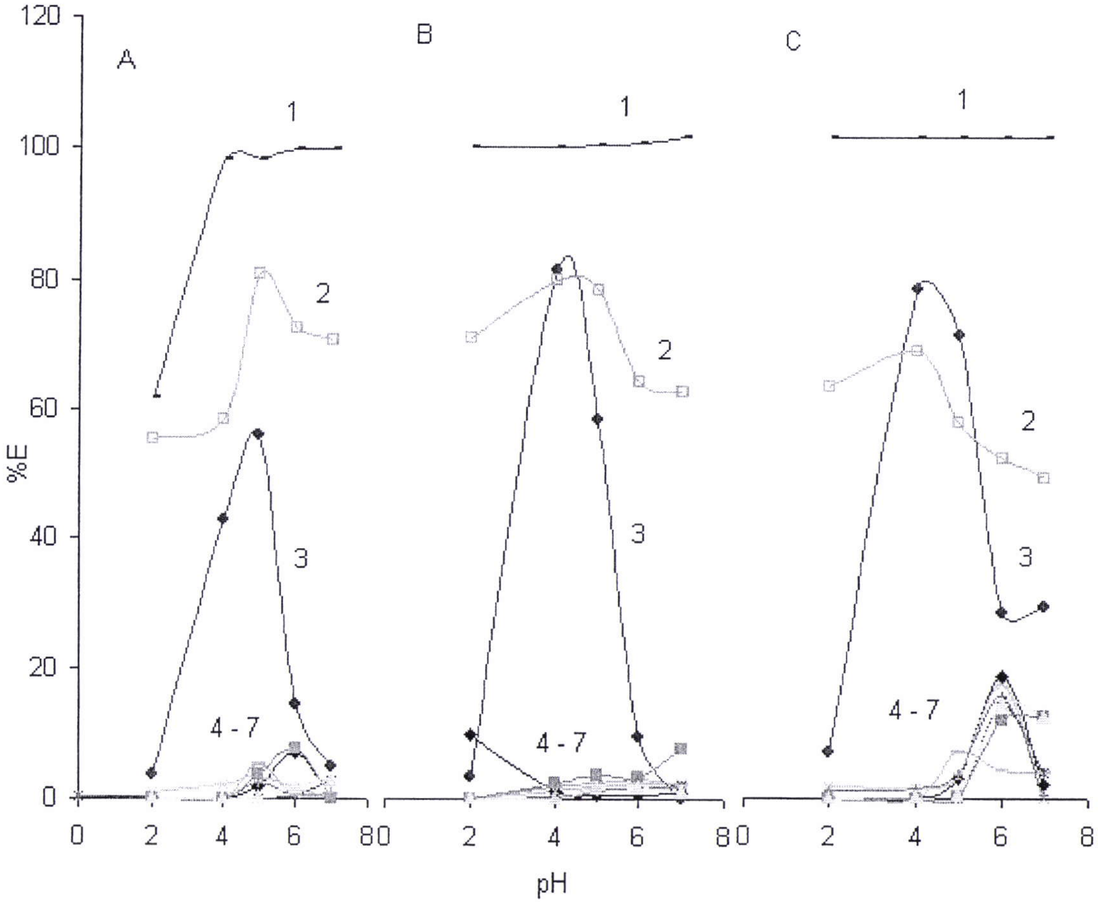

Fig.3. Effect of pH on the extraction of metal ions (1= Ag^{+}, 2= Hg^{2+}, 3= Cu^{2+}, 4-7= Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) with 2×10^{-4} M thiacrown ether (A= 12S4, B= 15S5, C= 18S6). Picrate concentration 1×10^{-3} M.

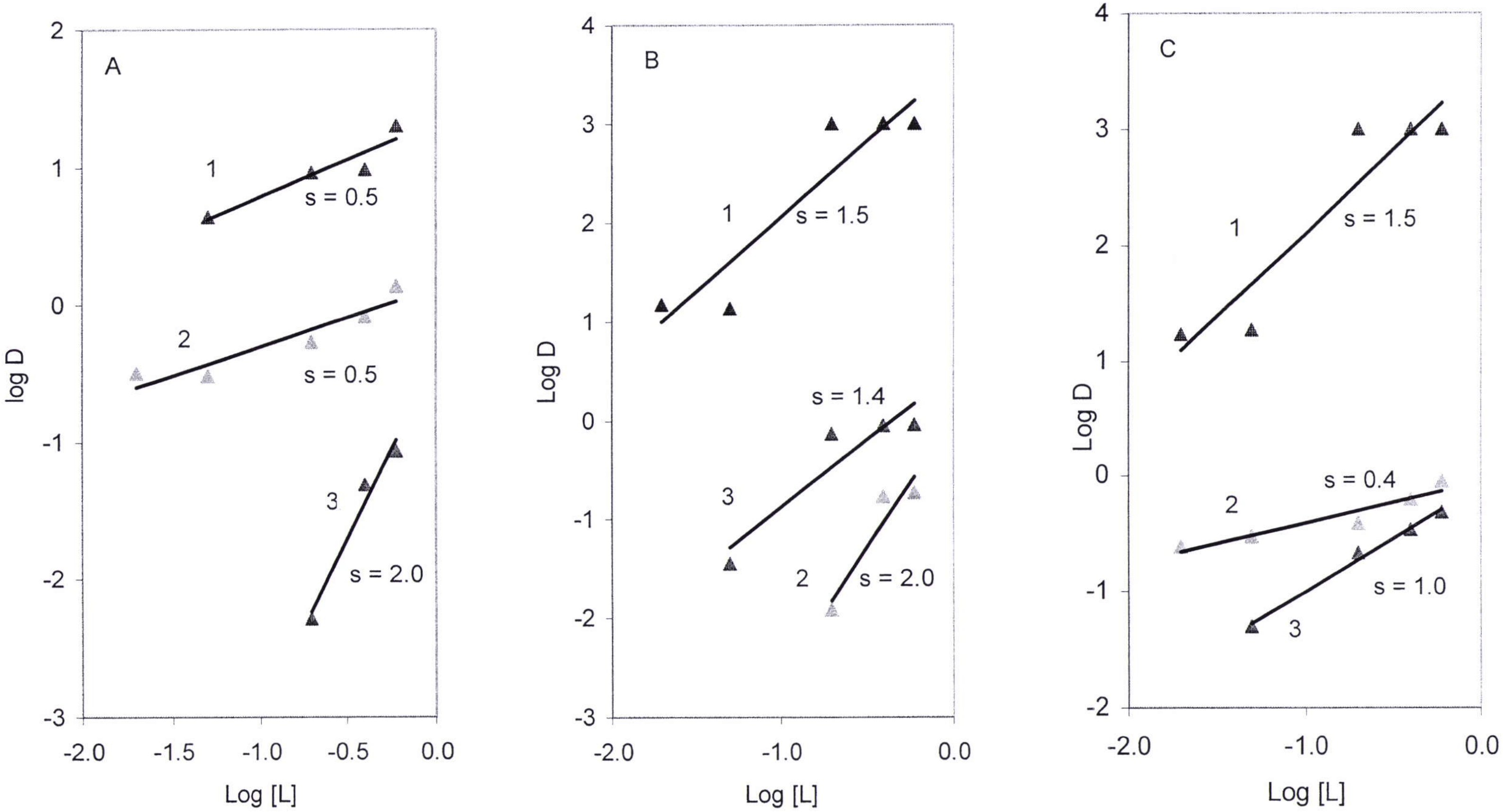

Fig.4. Effect of thiacrown ether (A= 12S4, B= 15S5, C= 18S6) concentration on the distribution ratio of metal ions (1= Ag^+, 2= Hg^{2+}, 3= Cu^{2+}) from picrate medium (1×10^{-3} M), pH (A= 5, B & C= 4), s= slope.

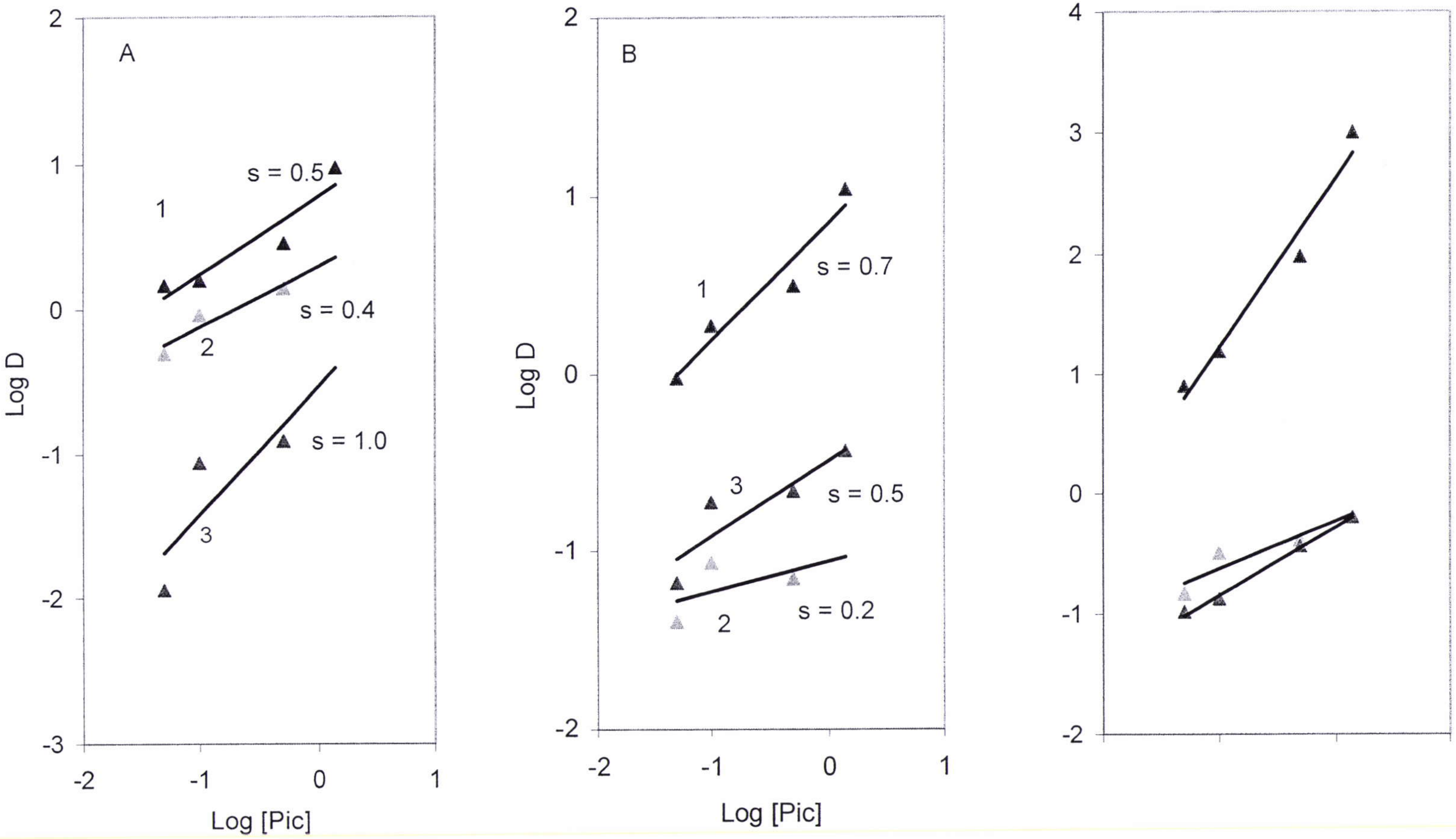

Fig.5. Effect of picric acid concentration on the distribution ratio of metal ions (1= Ag^+, 2= Hg^{2+}, 3= Cu^{2+}) with (2×10^{-4} M) thiacrown ether (A= 12S4, B= 15S5, C= 18S6), pH (A= 5, B & C= 4), s= slope.