

Temperature Effects on Solvent Extraction of Fe III , Co II , Ni II and Cu II with Thiourea Monophosphazene and Synergic Effect of Tributyl phosphate on Co II Extraction.

A.E. Arifien, A.H. Amrallah, R.M. Awadallah and S.M. Sirry
Chemistry department , Faculty of Science of Aswan, South Valley University,
A. R. Egypt.

Keywords: solvent extraction, synergism, thiourea monophosphazene.

SUMMARY

The extraction of the title ions from aqueous media with thiourea monophosphazene (H_2MPZ) has been examined in chloroform at three degrees of temperature. It was found that the temperature has no effect on the stoichiometry of the extracted species. The formation constant of the extracts were measured as a function of temperature to obtain the free energy, enthalpy and entropy changes. The thermodynamic functions were calculated and discussed together with the structure of the extracted species. Moreover; the synergistic effect of TBP on the extraction of Co II which has a low extractability was examined. The adduct formation was carried out and the results revealed that the rate and percentage of extraction were increased markedly.

INTRODUCTION

Although organophosphorus compounds containing P-O groups, i.e. phosphine oxides and tri-n-butyl phosphate (TBP) have long been in use for solvent extraction of transition metals⁽¹⁻⁴⁾. Thiourea monophosphazenes containing P-NH and C=S groups are novel compounds in this respect. Little information are available in using these compounds as chelating and extracting agents⁽⁵⁻⁷⁾. In our previous work⁽⁸⁾, the extraction of the title cations have been extracted by H_2MPZ in four different diluents⁽⁵⁾ and investigated in detail. On extending this investigation, the effect of temperature on the extraction and the mechanism of the extraction process were carried out and discussed on the light of the obtained results. The low extractability of Co II in chloroform in the previous work⁽⁸⁾ encourages us to test the neutral ester, TBP, as a synergic agent to enhance and increase the efficiency of Co II extraction.

EXPERIMENTAL

Chemicals and Reagents:

All chemicals used were of A.R. grade. The title reagent; 1-o-tolyl-2, 2-(dianilino)-2-(N-phenylthiourea) monophosphazene, H_2MPZ , was synthesized according to the procedure already described⁽⁹⁾. The product was recrystallized from ethyl alcohol to give a colorless crystals; m.p.207°C and elemental analyses;

C=68.9, H=5.52, N=12.4, P=6.8 and S=7.1. The analyses as well as the IR are in good agreement with the published data⁽⁹⁾. Tributyl phosphate was employed without further purification. Stock solutions of the two reagents 1×10^{-2} M in chloroform were prepared and diluted as required. Stock solutions of chloride salts of the title cations 1×10^{-2} M were prepared in bidistilled water and standardized by EDTA⁽¹⁰⁾. The ionic strength was adjusted for each cation by NaNO_3 . Buffer solutions were prepared as given by Britton⁽¹¹⁾ and Perrin⁽¹²⁾ and checked with pH-meter HI 8418 type.

Extraction and Analytical Procedures:

Equal volumes of both aqueous phase (10ml) containing (2 ml 1×10^{-4} M metal ion, 1 ml NaNO_3 , 7 ml buffer solution) and organic phase containing 1×10^{-4} M of H_2MPZ in chloroform were shaking in 50 ml stoppered conical flask using a thermostatic water bath (Gallenkamp) maintained at the required temperature 25°C . The optimum conditions of extraction were similar as represented earlier⁽⁸⁾, (pH=5.44, 9.5, 9.5, 7.0; ionic strength = 0.09, 0.09, 0.04, 0.025; equilibration time = 5, 20, 45, 20 min. for Fe III, Co II, Ni II and Cu II respectively). Following the equilibration, the two phases were separated and 5ml aliquots of the aqueous phase were pipetted out for metal ion analysis spectrophotometrically. The metal ions concentrations were measured on Shimadzu-240-uv.vis. spectrophotometer at λ_{max} 240, 500, 445 and 440 nm for Fe III⁽¹⁰⁾, Co II⁽¹³⁾, Ni II⁽¹⁴⁾ and Cu II⁽¹³⁾ respectively. The metal ion content in the organic phase was calculated as the difference between the starting solution concentration and the residual contents after equilibration.

It is worth mentioning that chloroform was used in this investigation because it is the best solvent for the extractant H_2MPZ . Also, the extraction of the considered metal ions in chloroform behaved differently in comparison with the other studied diluents⁽⁸⁾.

Results and Discussion

Extraction Isotherms :

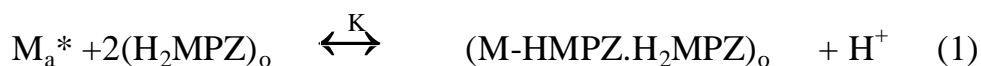
The extraction of Fe III, Co II, Ni II and Cu II from aqueous solution 2×10^{-4} M

each by $6 \times 10^{-4} \text{M}$ H_2MPZ in chloroform at constant pH and ionic strength (cf.expt.) and at various temperatures (20, 25 and 30°C) is shown in Figs.1&2 where $\log D$ was plotted vs. $\log (\text{H}_2 \text{MPZ})$. All the plot isotherms gave almost straight lines with a slope of two in case of Fe III and Cu II while in case of Co III and Ni II equal one. This suggests the participation of two or one molecules of $\text{H}_2 \text{MPZ}$ in the formation of the extracted species. It was found also that the slope of $\log D$ -pH plots for the four studied systems at constant ligand concentration ($1 \times 10^{-3} \text{M}$) was first order dependence on $[\text{H}^+]$. This means that only a single proton is liberated during the chelation process. A typical set of extraction data is depicted in Table 1. An error analysis of all the data indicated an expected extraction coefficient (D). The distribution ratios used in the calculation are the average values of triplicate runs.

Table 1. Distribution ratios and extraction efficiency of Fe III, Co II, Ni II and Cu II at 20 - 30°C by $[\text{H}_2 \text{MPZ}] = 6 \times 10^{-4} \text{M}$ and $[\text{M}^{n+}] = 2 \times 10^{-4} \text{M}$ at optimum conditions (cf. expt.).

$T^\circ\text{C}$	Fe III		Co II		Ni II		Cu II	
	D	%E	D	%E	D	%E	D	%E
20	9.00	90.00	1.22	54.95	1.86	65.03	2.57	71.99
25	3.17	76.99	1.86	65.03	4.32	81.20	3.00	75.00
30	2.57	71.99	4.00	80.00	5.66	84.98	4.26	80.99

In point of the data in Table 1 and Figs. 1&2, D increase markedly with rise in temperature in case of Co II, Ni II and Cu II with a beneficitation of extraction 21.6, 4.7 and 7.99% respectively in the range from 25°C to 30°C . This means that the extraction process is assumed to be endothermic whilst the extraction of Fe III does not favor higher temperature which means that the process is exothermic. The assumption made in analyzing the slopes of the straight lines obtained are: the activity coefficient is constant in solutions, hydrolysis and polymerization in aqueous and organic phases are absent and the side reaction doesn't occur. According to the above finding results, the over all extraction equilibrium could be represented as follows:



where a and o denote aqueous and organic phases respectively, M^* stands for Fe III or Cu II and M_a for Co II or Ni II.

It should be mentioned that the obtained results reflect that, the temperature has no effect on the stoichiometry of the extracted complexes. Also, the stoichiometry appeared in the above equations are in agreement with the molar ratio and continuous variation methods which were applied in this connection. Further more, in order to confirm the composition of the extracted species and the status of the anion of metal salts used, the organic phase after careful separation was allowed to evaporate and digested with fuming nitric acid. The digested solution was tested for Cl^- which gave +ve result in case of Co- H_2 MPZ complex while the other metal complexes were -ve . This check was ascertained together with the composition of the solid complexes by elemental analyses and molar conductance measurements of $1 \times 10^{-3} \text{M}$ of complexes in ethanol which were in good agreement with the reference values⁽¹⁵⁾, (cf .Table 2).

Table 2. Some physical and chemical characteristics of M- H_2 MPZ complexes.

Complex	M.P.	$\Lambda \text{ ohm}^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$	Element Analysis Found (calcd.)			M. W.
			%C	%H	%N	
$\text{Cu}(\text{H}_2\text{MPZ})_2 \cdot \text{H}_2\text{O}$	217	70	60.90 (60.95)	5.20 (5.32)	13.60 (13.69)	1024.6 (1022.55)
$\text{Ni}(\text{H}_2\text{MPZ})_4 \cdot \text{H}_2\text{O}$	220	39.9	52.00 (51.92)	5.60 (5.70)	11.90 (11.64)	608.3 (601.51)
$\text{Fe}(\text{H}_2\text{MPZ})_2 \cdot 4\text{H}_2\text{O}$	245	72	57.92 (58.4)	4.83 (4.77)	13.21 (13.10)	1059.3 (1068.90)
$\text{Co}(\text{H}_2\text{MPZ})(\text{CHCl}_3)_4 \cdot 6\text{H}_2\text{O}$	230	35	30.80 (31.29)	3.50 (3.68)	6.70 (6.08)	1151.65 (1112.18)

Thermodynamic Parameters and Mechanism:

The extraction constant (k_{ex}) for the studied complexes were calculated from the equilibrium metal concentration in the organic and aqueous phase according to equations 1 and 2. From the values of (k_{ex}) at the temperature range investigated, vant'sHoff equation was used to calculate the enthalpy change (ΔH) by plotting $\ln k_{\text{ex}}$ against the reciprocal of absolute temperature (Fig.5) where the slope equals $-\Delta\text{H}/\text{R}$. From these values, it could then be used to obtain

the corresponding free energy and entropy changes (ΔG , ΔS). The data are summarized and given in Table 3. The error limits of these values are estimated to be about 1% for ΔG and 3% for ΔH and ΔS .

The thermodynamic data depicted in Table 3 can be explained on the bases of two factors associated with the process of extraction namely, i- the dehydration of the metal cation and the hydration of the released protons, ii- the combination of metal cation and ligand anion in the organic phase and the simultaneous deprotonation of the formed chelates.

Table 3. Thermodynamics values for the extraction of Fe III-, Co II-, Ni II- H₂MPZ complexes and Cu II .

Metal ion	1/T.10 ³	ln k _{ex}	ΔH^a	ΔG^b	ΔS^c
Fe III	3.41	3.47	-0.015	-2.192	7.31
	3.36	3.42			
	3.30	2.60			
Co III	3.41	-14.26	0.020	8.11	-27.14
	3.36	-13.90			
	3.30	-13.10			
Ni II	3.41	-13.84	0.021	7.76	-25.97
	3.36	-13.00			
	3.30	-12.67			
Cu II	3.41	-0.33	0.009	0.14	-0.44
	3.36	-0.18			
	3.30	-0.21			

a= k cal./mol

b= k cal./mol

c= cal./deg./mol

Thus, the sequence of +ve ΔH values; Ni > Co > Cu suggests that the dehydration process predominates and this anticipated order will be more or less inversely parallel to the hydration energy of the metal ions⁽¹⁶⁾. Concerning the entropic contribution, the literature data⁽¹⁷⁾ in similar cases show that the degree of order which lost during the dehydration of the cation is not compensated by the order caused by the hydration of the proton. Thus, it is reasonable to assume that the entropic contribution in the organic phase is ruled by the degree of order which is gained as a consequence of the highly ordered chelate structure which is formed between the metal ions and the thiourea monophosphazene ligand.

Therefore, the ve ΔS values are justified.

Synergistic Extraction of Co II by H₂MPZ and TBP:

The data obtained in Table 1 reveal that the efficiency of extraction of Co II by monophosphazene at 25°C is relatively low as compared to the other studied metals (65.03%). So, TBP was used in the present study as a trial to improve, enhance and increase this efficiency.

Test of Synergism:

Initially, to ascertain whether a synergic effect was obtainable distribution coefficient of Co II was carried out using variable concentrations of both H₂MPZ and TBP mixtures having 1×10^{-3} M total concentration. All measurements were adjusted at 0.09M ionic strength and pH 9.5 in chloroform. The results revealed that the maximum synergism took place at equimolar ratio of both extractants and the metal ion.

Equilibration Period :

Distribution experiments were performed to measure the period required for equilibrium distribution of Co II when using TBP together with H₂MPZ. The extraction concentration mixture and the experimental conditions were similar to those employed in synergistic test. The obtained results gave a maximum extraction after 15 min. shaking. Thus, the rate of extraction was enhanced and the efficiency increased to reach 92.5% as compared with the binary extraction of Co II (cf. fig.4).

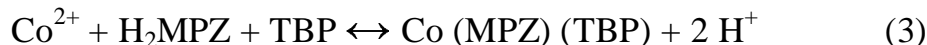
Mechanism of the Synergistic Extraction:

The synergistic effect is expected to be caused by a formation of more soluble complex in the organic phase than the simple complex Co (H₂MPZ). So, the determination of composition of the adduct complex is necessary in order to elucidate the synergistic extraction mechanism.

To obtain information on the possible species being extracted into the organic phase, the three variables in the system [H⁺], H₂MPZ and TBP where examined keeping two constant at a time. It was found that on keeping H⁺ and TBP concentrations constant, while varying the H₂MPZ concentration, a log D against log [H₂MPZ] plot produced a straight line of slope one (Fig.4) . A similar log /log plot varying only H⁺ gave a line of slope two (Fig.5). Also, plotting log D vs. log [TBP] at constant H⁺ and H₂MPZ concentrations gave a

straight line with slope one . That is, one molecule of both H₂MPZ and TBP is participated in adduct formation with releasing of two protons.

From the above results we assume the reaction goes according to the equation:



and the synergic extraction is given by:

$$K_{\text{syn}} = \frac{[\text{Co}(\text{MPZ})(\text{TBP})][\text{H}^+]^2}{[\text{Co}^{2+}][\text{H}_2\text{MPZ}][\text{TBP}]} \quad (4)$$

and the distribution constant of the metal in the synergic system by

$$D_{\text{syn}} = \frac{[\text{Co}(\text{MPZ})(\text{TBP})]}{[\text{Co}^{2+}]} \quad (5)$$

therefore,

$$K_{\text{syn}} = \frac{D \cdot [\text{H}^+]^2}{[\text{H}_2\text{MPZ}][\text{TBP}]} \quad (6)$$

The D values for the individual ligands were obtained at the same experimental conditions and were found to be 1.5 and 8.09 for H₂MPZ and TBP respectively.

According to equation 3, one mechanism can be assumed that this synergic effect is due to the addition of the nonionic molecule TBP through hydrogen bond to the extracted species CO- H₂MPZ. So far, there is inadequate experimental support for this hypothesis. The other mechanism is proposed that an aqua-metal-H₂MPZ complex such as Co.H₂MPZ.H₂O is rendered less hydrophilic by the substitution of the neutral ester TBP for the water group such as Co.H₂MPZ.TBP. In such a complex the neutral ester would probably be attached through its P=O bond to H₂MPZ. Supporting evidence for this mechanism comes from the macro isolation of the water insoluble crystalline Co-H₂MPZ-TBP solid complex with approximately the expected metal / H₂MPZ/TBP mole ratios which appear to contain practically no water. This does not preclude the possibility of formation of some metal/ H₂MPZ /TBP complex which have retained some water of constitution in their complex. If one assume that H₂MPZ and TBP have bi-and mono- dentate bonds respectively with Co II through NH-C=S and P=O bonds, then one would expect some interaction between H₂MPZ and TPB in the absence of the metal. This expectation was obscured since the absorption spectra of H₂MPZ which has two

characteristic bands at λ 243 and 278 nm. in chloroform was persisted without alteration in presence of TBP. The IR study together with the absorption spectra and water contents of organic phase and solid complexes of the adduct will be the subject of subsequent work.

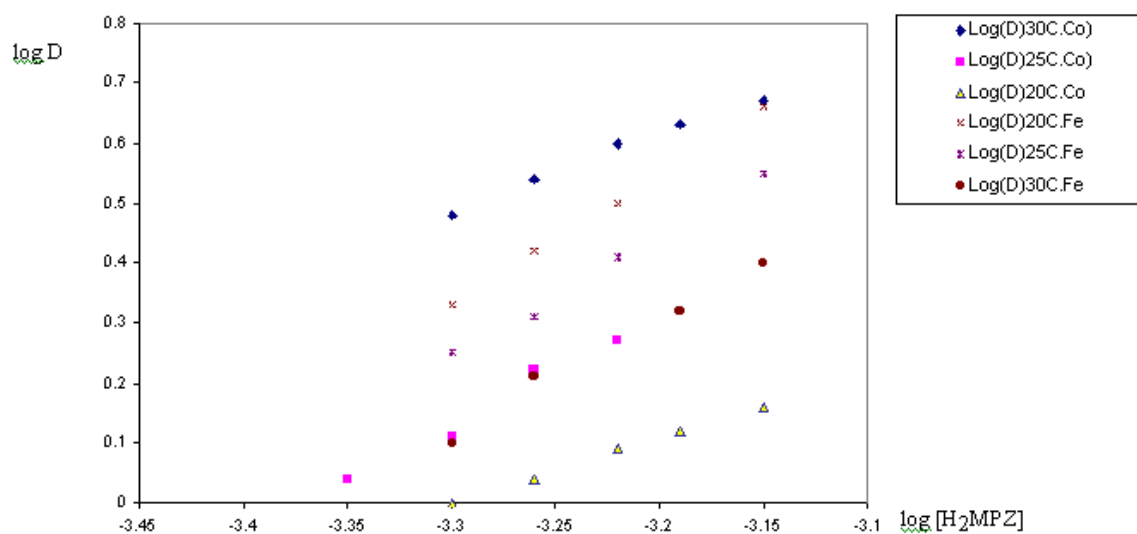


Fig.(1)- Effect of [H₂MPZ] on the extraction of Ni II and Cu II in chloroform at 20, 25 and 30°C at the optimum conditions.

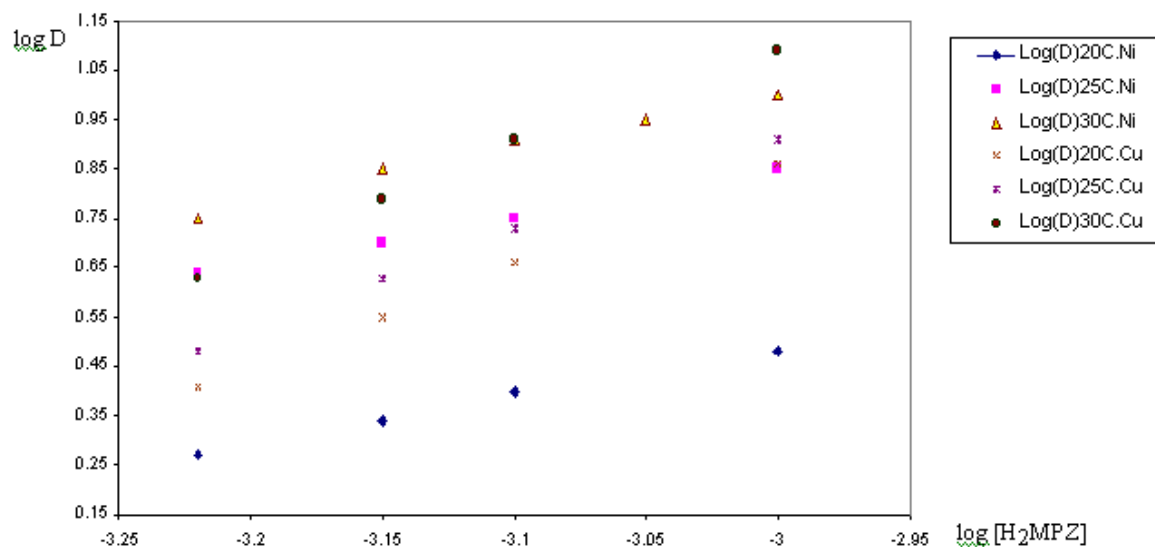


Fig.(2)- Effect of [H₂MPZ] on the extraction of Fe III and Co II in chloroform at 20, 25 and 30°C at the optimum conditions.

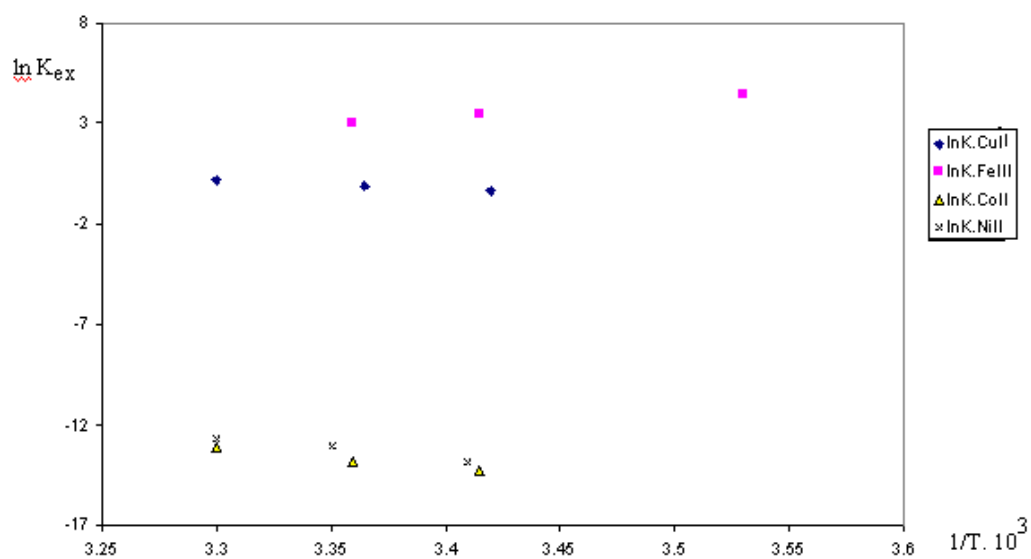


Fig.(3)- Temperature dependence of extraction of Fe III, Co II, Ni II and Cu II with [H₂MPZ] in chloroform.

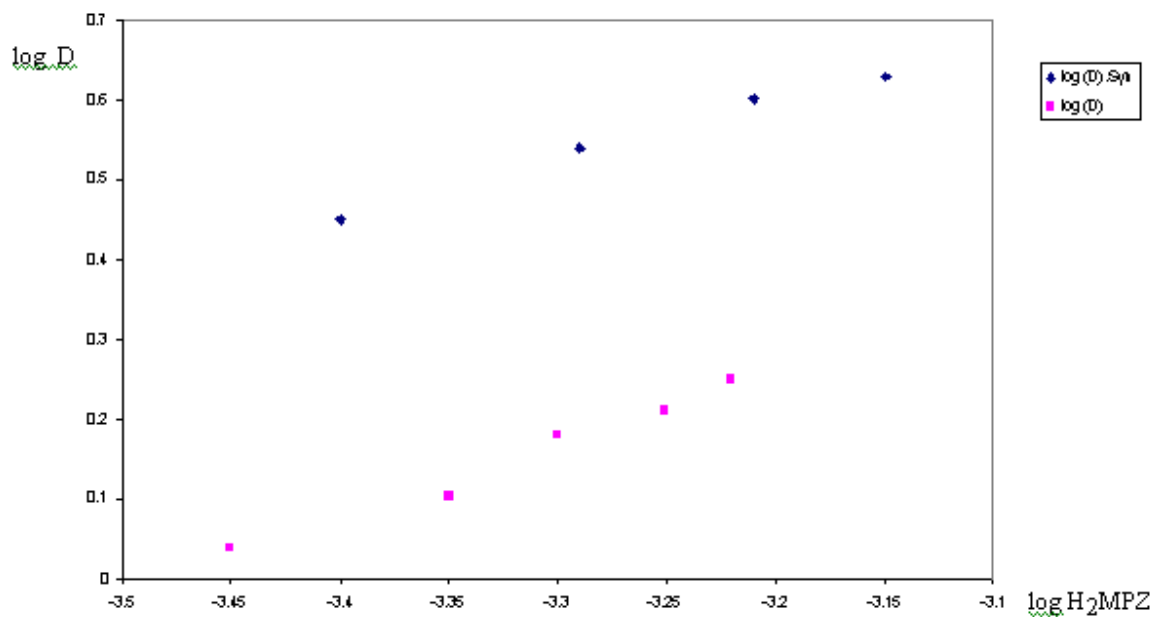


Fig.(4)- Extraction of Co II by[H₂MPZ] without TBP , log D , and in presence of constant [TBP] (5×10^{-4} M) , ($\log D_{\text{syn}}$), in chloroform at 25^o C.

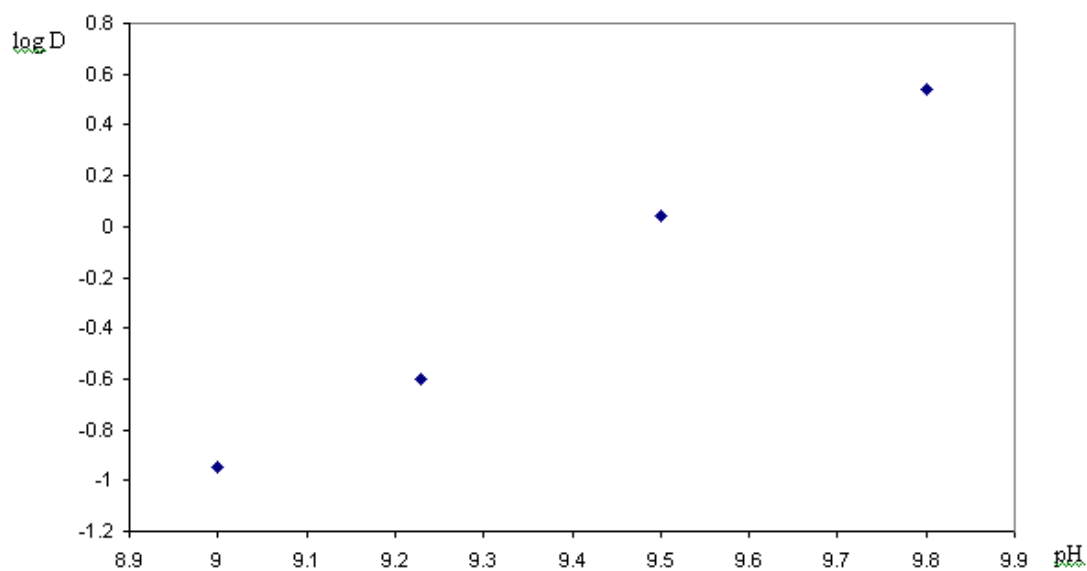


Fig.(5)- Effect of pH on the extraction of Co II by [H₂MPZ] and TBP 5×10^{-4} M, in chloroform at optimum conditions (cf. expt.).

REFERENCES

- 1- A. K. De and M.S. Rahman, *Talanta*, 11,601-6 (1964).
- 2- A. K. De "solvent extraction of metal "Van Nostrand Reinhold Co. (1970).
- 3- T.A. Handly and J.A .Dean, *Anal. Chem.*, 3463 (1962).
- 4- J.W.O' Laughlin and C.V. Banks, U.S-At. Energy Comm. Rept. IS-737 (1963).
- 5- A. E. Arifien and E.H.M. Ibrahim, *Polish J.Chem.* 56, 41,(1981).
- 6- A. E. Arifien, *Pakistan J.SC.Ind.Res.* 77(3),127,(1984).
- 7- A.E. Arifien, *Bull. Fac. Sci., Assuit Univ.*, 19(2-B), 57(1990).
- 8- A.H. Amrallah, A.E. Arifien, R. M. Awadallah and S. M. Sirry, *Bull, Fac. Sc., Assiut Univ.*, 24 (2-B), 57-82 (1995).
- 9- E.H. Ibrahim and A.S. Lashine, *Indian J. Chem.*, 18B, 368 (1979).
- 10- A.I. Vogel," *A Text Book of Quantitative Inorganic Analysis*", Longman, 4th Ed. (1982).
- 11- H.T.S. Britton, "Hydrogen Ions ", D. Van Nostrand company 4th Ed., Vol. I (1965).
- 12- D .D. Perrin and Boyed Demposey, "Buffers for pH and Metal Ion Control", Chapman and Hall , London (1974).
- 13- J. Fries, H. Getrost "Organic Reagent For Trace Analysis" B. Meock, Darmstadt (1977).
- 14- V.A. Posypaisko and N.A. Vasina "Analytical Chemistry in Metallurgy"(1984).
- 15- W.L. Geary, *Coord. Chem. Rev.*, 7 , 81 (1971).
- 16- F.Basolo and R.G. Pearson "Mechanisms of Inorganic Reactions", John Wiley & Sons Inc., New York (1963).
- 17- B. Manke KC., "Electrolytic Dissociation", Academic Press, New York (1961).