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Organic Solvent Effect, Thermodynamic Study and Synergism Behavior for Extraction Efficiency of Cobalt (II) Complex with 1-[2-Pyridyl Azo] -2-Naphthol.

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Abstract- After pinpoint all optimum conditions for extraction Cobalt(II) as ion pair association complex or chleated complex with complexing agent 1-[2-pyridyl azo] -2-naphthol which dimonirtrate λ_{max} for complex extracted was (446nm.) more stable complex formation was at pH= 7 and 60 μg Co(II)/5ml with 1×10^{-4} M 1-[2-pyridyl azo] -2-naphthol[PAN] dissolved in chloroform and shaking time 10 minutes. The stoichiometry of complex extracted to the organic phase was 1:1 metal : PAN $[Co(PAN)^{+}Cl^{-}]$ or $[Co(PAN)]^{+}(Cl^{-})$.Extraction method was endothermic as well as thermodynamic parameters after calculated was ΔH_{ex}= 0.0149 KJmol^{-}, ΔG_{ex}= -58.81 KJ mol^{-} and ΔS_{ex}= 176.55 J mol^{-}. Synergism study show from the slope is appear there is one molecule of TBP or MIBK participated in the structure of complex extracted to the organic phase.

I. Introduction

The phenomenon in which two extractants when present together, extracted species, mostly metal ionswith greater efficiency than that corresponding to their additive action is called synergism. Rather much effort has been devoted to synergistic extractions over the past two decades since the very nature of synergism offers interesting research possibilities of both the chemistry of these extractants and their potential application[1].

Functions of cobalt , enters in the composition of vitamin B12 and contributes to the metabolism of carbohydrates, proteins. Produces amino acids and creates DNA molecules. Supports the immune system and the nervous system in their work. Responsible for keep the work of the cells and the growth and development of red blood cells. High dosage of cobalt affects the heart may reduce a man's fertility. Cobalt sources, cobalt found in fruits and vegetables, but our body prefers cobalt content in vitamin B12, so it prefers to depended on this vitamin to secure our need of cobalt .Adults need2.4 micrograms of vitamin B 12 to ensure access to cobalt, and supplements should not exceed 1.4 micrograms of leafy vegetables containing 20-60 micrograms of Cobalt . While 100 grams of meat containing 15-25 micrograms of cobalt[2,3].

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Solvent extraction in an indirect separation method in general depend on thermodynamic laws, as well as from the other hand less depend on kinetic laws, and from this truth we must know all effective parameters on extraction efficiency according to this method. Kokade et al extracted Bismuth(III) by n-octyl aniline dissolved in chloroform from HCl and HBr media, and the study demonstrate the ion pair complex extracted was (RNH_3^{+}) $BiCl_5^{-2}$[4], anther researchers were perform to separation of Sn, Sb, Bi, Al, Cu, Pb and Zn from hydrochloric acid solution by solvent extraction process using TBP as an extractant[5]. A new research for extraction, determination of Manganese by using cloud point extraction, this research include formation ion pair association complex between brilliant green and MnO_4^{-} in acidic media, and this complex extracted to surfactant Triton X-100. The cloud point layer contain ion pair complex dissolved in alcohol and measure the absorbance at λ_{max} = 657nm[6]. Extraction, separation and preconcentration of Nickel (II) as chloroanion by using crown ether DB18C6 according to CPE method, and absorbance spectrum forion pair association complex extracted illustrate λ_{max}= 295nm., as well extracted good efficiency was at 0.5 M HCl and 0.25M NaCl and 1×10^{-4} DB18C6[7]. A new trend in extraction and preconcentration of chromium(VI) using laboratory made-Azo dye reagent 2-[benzene thiozolyl azo]-4-benzene naphthol (BTABN) after cloud point extraction(CPE) and its determination by spectrophotometriclly, the method involved the reaction of $Cr_2O_7^{=}$ with (BTABN) in acidic medium forming a hydrophobic ion association complex $[HBTARN^{+}][HCr_2O_7^{-}]$ which is entrapped into micelle-mediating solvent (Triton X-100) and the Cr(VI) detected spectrophotometriclly at λ_{max}=475 nm[8]. In research for extraction chloro anion complex of Cd(II) and Hg(II) used many organic agents as extractant according to liquid ion exchange method such as extractant α-naphthol amine, 4-amino benzoic acid, 2-[(4-(Carboxy methyl phenyl) azo]-4,5-diphenyl imidazole and Cryptand C222, this study includes definition hydrochloric acid concentration in aqueous phase and shaking with organic phase necessary for extraction[8]. 2-[4-(Chloro-2-methoxy phenyl) azo]-4,5-diphenyl

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imidazole used as a new complexing organic reagent for extraction and determination of Copper(II) in different samples at optimum condition[9]. Determined Cupper at trace level by using 1- nitroso-2- naphthol as complexing agent in presence of anion aqueous micellar solution of 1% sodium dodecyl sulphate. The complex extracted was Cu:$(NNph)_2$[10]. Extracted Mo(VI) from 2M HCl by solvent extraction with 2-n-Octyl amine pyridine in prescience Lithium Chloride as salting agent[11]

II. Instruments

All spectrophotometric measurements and absorbance were registered by using a double beam (UV-Vis) spectrophotometer Shimadzu UV 1700 (Japan) and a Single beam (UV-Vis) spectrophotometer TRIUP international corp. TRUV 74,S (Italy), . Shaker used HY-4 vibrator with adjust about speed multiple(Italy).pH-meter WTW-INOLAB made in Germany.

III. Materials

All chemicals used provided from Fluka and Merck such as Cobalt chloride six hydrate , ammonia, sodium hydroxide, chloroform, hydrochloric acid,1-Nitroso-2-naphthol., But 1-[2-pyridyl azo] -2-naphthol[PAN] was prepared as in [12].

IV. Experimuntal

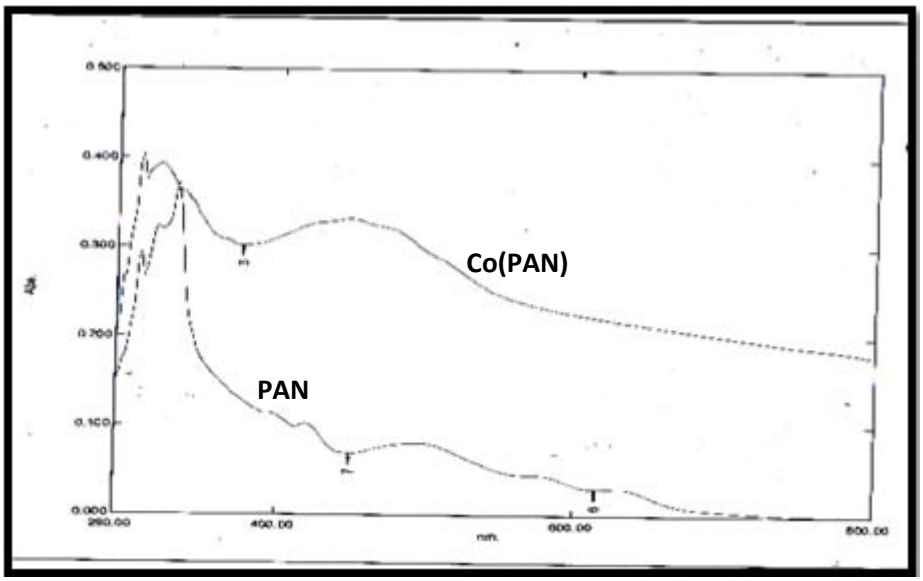
All chemical used were of A.R grads and used as received with out farther more purification, all solution prepared with doubly distilled water, stock solution of Cobalt(II) was prepared by dissolved 0.45 gm of $CoCl_2$.$6H_2O$ in 100 ml doubly distilled water contain 1ml concentrated HCl also by diluting with doubly distilled water prepared other work solutions .For determination Cobalt(II) in aqueous solutions used 0.5% solution of 1-Nitroso-2-naphthol dissolved in glacial acetic acid according to the procedure detailed in [13].Derivative 1-[2-pyridyl azo] -2-naphthol(PAN) prepared a solution of 1×10^{-4} M by dissolved 0.0249 gm in 100 ml chloroform in volumetric flask.

V. Procedure

Solvent extraction of Cobalt(II) as complex with (PAN) to apply by taken 5ml aqueous solution contain fixed concentration of Cobalt(II) atpH =7 with 5ml of 1×10^{-4} M of (PAN) dissolved in chloroform ,shake the two immiscible layers for 10 min after that separate the two layers and measure the absorbance of organic phase against PAN solution at λ_{max}=446 nm. And the aqueous phase treated according to 1-Nitroso-2-naphthol method[13] and returning to calibration carve in Fig(2) to determine remainder quantity and the quantity of Cobalt(II) transferred to the organic phase to produce the complex, afterward calculate distribution ratio D of extraction.

VI. Results and Discussion

The spectrum of complex to be formed in organic phase which is in Figure(1)Show λ_{max} =446 nm, and used this wave length to measure the absorbance of complex formed and transferred to the organic phase.



(1) UV VIS spectrum of PAN and Co(PAN)complex

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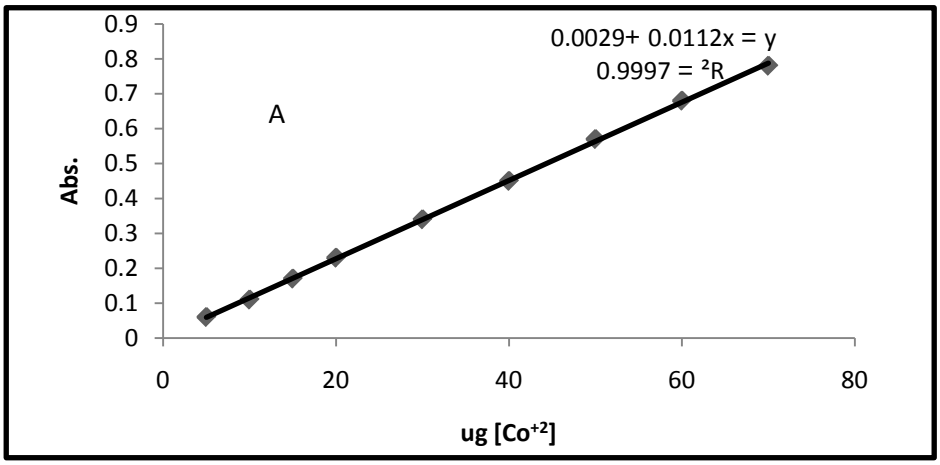
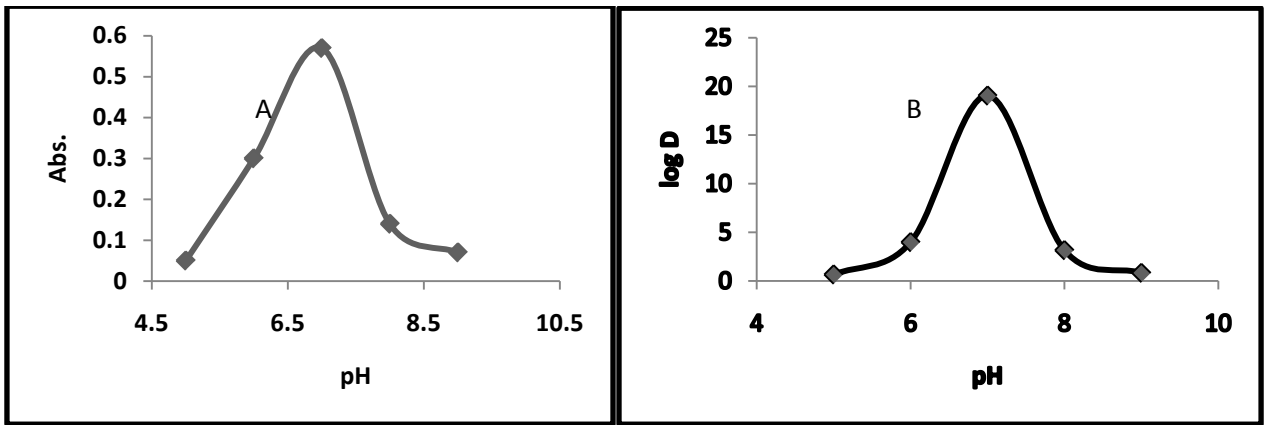


Fig(2) : Calibration curve for determination Co(II) in aqueous solution by1-Nitroso-2-naphthol

VII. Effect of pH

5ml aqueous solution contain 60ug Co(II) at different pH(5-9), add to each solution 5ml of 1×10^{-4} M of (PAN) dissolved in chloroform, and shaking the two immiscible layers for 10 minute, at latter separate organic phase from aqueous phase and measure the absorbance of organic phase against PAN solution as blanck and the aqueous phase for each solution treated according to 1-Nitroso-2-naphthol method[13],and returning to calibration curve Fig(2) to calculate distribution ratio D for all solutions of different pH. The results obtained was as in Figure (3)



Fig(3) : Effect of pH(A)on complex formation (B) pH effect on D values

VIII. Effect of Metal ion Concentration

Aqueous solution 5ml in volume contain different quantity of Co(II) (5ug-100ug) at pH =7, added 5ml of 1×10^{-4} M of (PAN) dissolved in chloroform, each solution shaking for 10 minutes, and after ending the shaking separate the two layers, and measure the absorbance of each organic phase at 446 nm against PAN solution as blank, and the aqueous solution treated according to 1-Nitroso-2-naphthol method[13], and after returning to calibration curve Fig(4) calculate D values.

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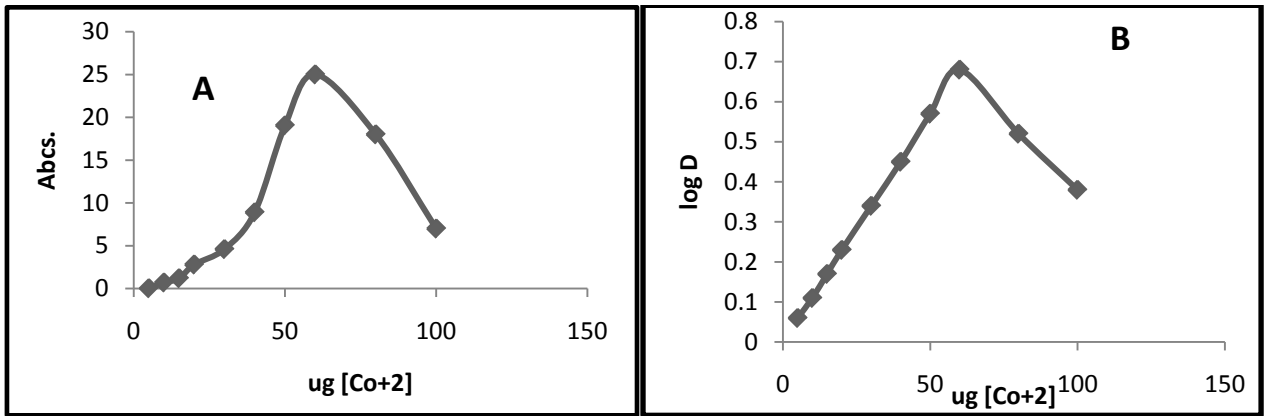


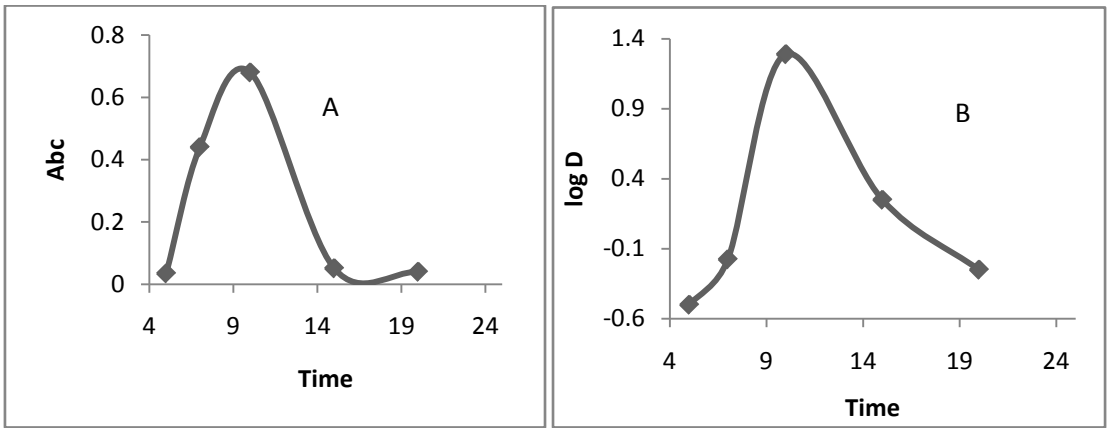
Fig (4) A : Absorbance differ as function of Co(II) concentration in organic phase B: Effect of metal ion concentration in aqueous phase on distribution ratio D

The results demonstrate 60 ug Co(II)/ 5 ml aqueous solution was the optimum concentration value of metal ion giving higher absorbance for complex formed in organic phase as well as higher distribution ratio D.

By the reason of metal ion concentration was a thermodynamic data effect on the thermodynamic equilibrium for complex formation and extraction efficiency, form this truth any concentration of Co(II) less than 60 ug/5 ml not allow to reach thermodynamic equilibrium and giving decrease in absorbance of complex organic phase and D values, as well as any Co(II) concentration more than optimum 60 ug effect to increase back reaction of equilibrium and dissociation complex according to mass action law and Le Chatelier principle.

IX. Shaking Time Effect

Extraction Co(II) from aqueous solutions 5 ml in volume contain 60 ug/5 ml at pH =7 with 5 ml of 1×10^{-4} M of (PAN) dissolved in chloroform after shaking these solution for different time (5-20 min), afterword determine absorbance of organic phase distribution ratio D for the solution at each shaking time, the results obtained was as in Fig(5):



Fig(5) A : Effect on shaking time of complex formation,(B) Effect of shaking time on D values

The results show 10 minutes was the best time for shaking which is giving higher absorbance for organic phase and higher value of distribution ratio D that is mean in this time of shaking time reached to the best thermodynamic equilibrium for complex formation and extraction, but any shaking time less than 10 minutes not enough to reach thermodynamic equilibrium giving decrease in absorbance and D value as well as shaking time more than 10 minutes effected to decline absorbance and D value by increase the rate of dissociation of complex.

X. Stoichiometry

To knowledge the structure of complex formed between Co(II) and PAN follow two spectrophotometric methods (mole ratio method, continuous variation method) , the two methods show the structure of complex was 1:1, metal: ligand that is mean the complex is ion pair association complex $[Co(PAN)]^{+}Cl^{-}$ or chelate complex $[Co^{+2}(PAN)^{-}(Cl)^{-}]$:

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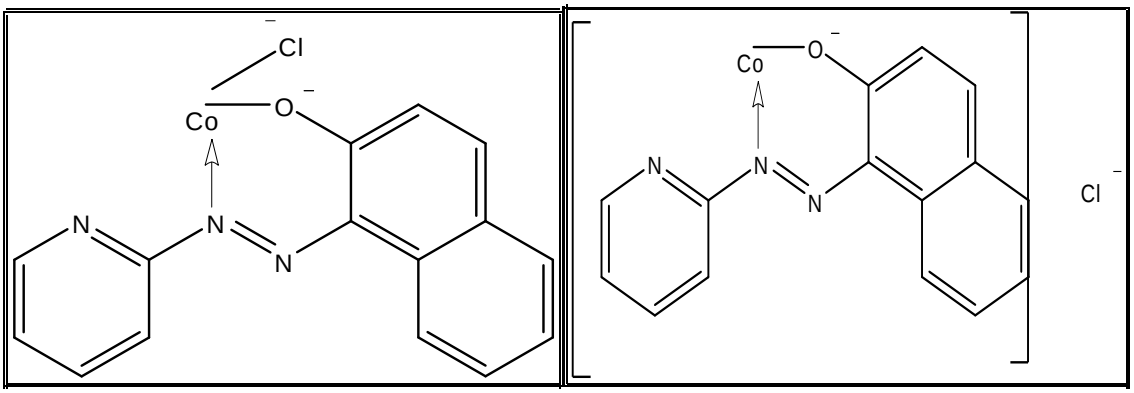


XI. Organic Solvent Effect

Extraction Co(II) from aqueous solution 5 ml in volume contain 60 ug dissolved in different organic solvent differ in dielectric constant, after shaking and separating and determine absorbance and D values the results was as the Table(1):

Table(1) : effect organic solvent on solvent extraction of Co(II)

Organic solvent	dielectric constantε	-ΔGTKJ mol^{-}	K_A10^{+4}	D	$K_{ex}10^{+8}$	$-\Delta G_{ex}$ KJmol^{-}
Nitro benzene	35.74	0.0424	18.05	4.81	15.94	51.36
Amyl alcohol	15.80	0.1412	48.43	8.66	43.3	53.76
1,2-D chlorɔ ethane	10.650	0.2263	27.69	6.39	23.94	53.32
Ch orobehzen	5.708	0.4523	387.59	25	372.08	58.47
Chloroform	4.808	0.5433	59.35	9.55	53.63	64.96
Benzene	2.804	0.9566	34.47	7.15	30.51	52.88
Toluene	2.438	1.1056	34.59	7.16	30.32	52.89

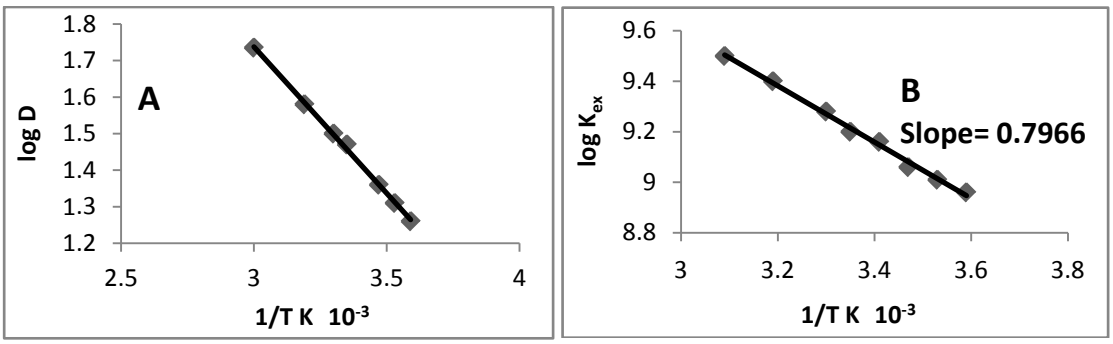
The results in Table (1) demonstrate there is not any relation between dielectric constant of organic solvent and distribution ratio values of extraction but there is unaffected for organic solvent structure as well as this results reflect participation of organic solvent in the formation of ion pair complex extracted, and chloroform organic solvent giving higher distribution ratio.

XII. Effect of Temperature and the Thermodynamic Study

Aqueous solution in 5 ml volume contains 60 ug Co(II) at pH =7 axtracted with 5 ml of 1×10^{-4} M (PAN) dissolved in chloroform at different temperature (5-60)C° after separated the two layers determine, distribution ratio D at each temperature, and calculate extraction constant K_{ex} at each temperature by application the relation below:

$$K_{ex} = \frac{D}{[Co(II)]_{aq}\,[PAN]_{org}}$$

The result shown in the Fig(6):



Fig(6) : (A) Effect temperature on distribution ratio D,(B) Effect temperature on extraction constant $K_{ex.}$

The results show the extraction method was endothermic as well as thermodynamic parameters after calculated was:

ΔH_{ex}= 0.0149 KJmol^{-}

ΔG_{ex}= -58.81 KJ mol^{-}

ΔS_{ex}= 176.55 J mol^{-}

The high value of entropy reflect the combination metal ion Co(II) with negative charged PAN

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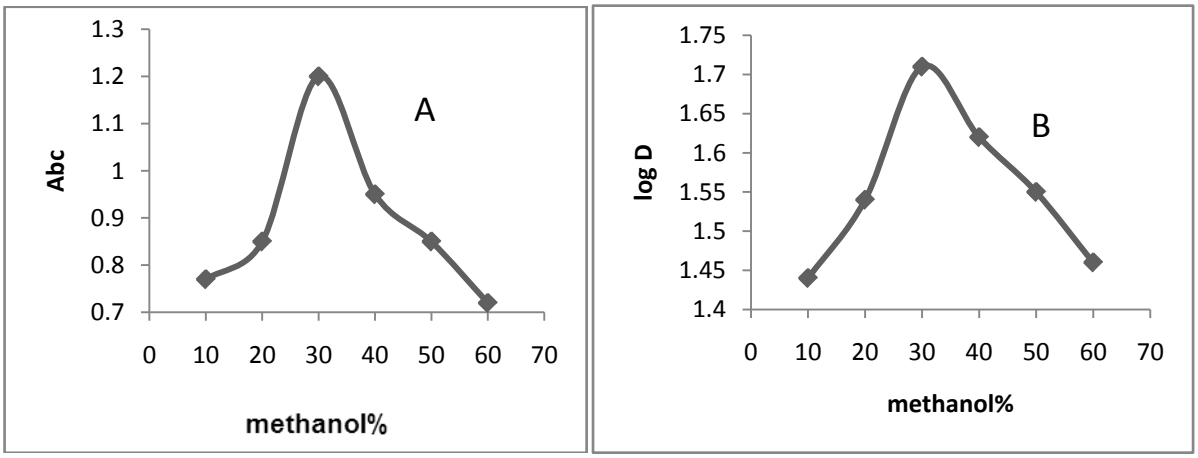
molecule at pH= 7 to approach one another with temperature rising which is help to increase in destroyed hydration shell and giving more stable complex extracted to organic phase as well as this reflect the extraction method is entropic in region.

XIII. Methanol Effect

Extraction Co(II) from aqueous solution 5 ml in volume contain 60 ug metal ion at pH =7 with different percentage of methanol 10% - 60%, with 5 ml of 1×10^{-4} M (PAN) dissolved in chloroform after shaking these two layers for 10 minutes, after finishing shaking separate the two layers and measure the absorbance of organic phase and calculate D values at each percentage of methanol . The results was as in Fig (7):



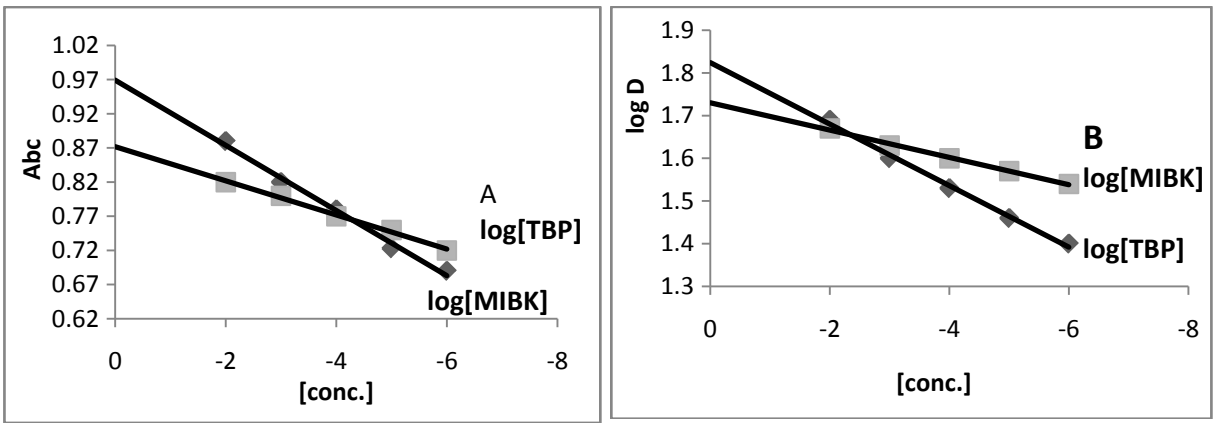
Fig(7) A : Methanol effect on complex formation, B: Methanol effect on D values

The results demonstrate presence methanol in aqueous solution effect to increase extraction efficiency until reached to the optimum quantity of methanol in aqueous phase, more than this value effect to decline efficiency of extraction as well as at very high percentage of methanol effect to decrease absorbance of organic phase and D values less than values in the case of without methanol, and the optimum value of methanol in procedure is 30%.

These results demonstrate methanol help in aqueous solution to destroyed the hydration shell of metal ion Co(II) so lone pair electron in function position of PAN molecule this destroyed increase as a function to percentage of methanol in aqueous solution to reacted maximum effect in 30% methanol more than 30% effect to decrease polarity of water this behavior effect to partition PAN molecular to the aqueous phase and decrease extraction efficiency to organic phase .

XIV. Synergism Effect

Extraction Co(II) from 5 ml aqueous solution contain 60ug Co(II) at pH =7 by 5 ml of 1×10^{-4} M (PAN) dissolved in chloroform contain different concentration(1×10^{-3} M - 1×10^{-6} M) from tributyl phosphate (TBP) or methyl isobutyl ketone, after shaking and separating the two layers determine absorbance of complex to the organic phase and D-values. The results was as in Figs (8).



Fig(8) A : Effect [TPT]&[IMBK] on complex formation, B: Effect of [TPT]&[IMBK] on D- values

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The results shows the absorbance and D. values in presence of TBP or MIBK was higher than in the case of absents TBP or MIBK and for all concentrations because TBP or MIBK participate in the complex formation by displacement TBP or MIBK molecules instead of water in the coordination shell of the metal ion Co(II) this giving more stable and more hydrophobicity for the complex and increase in the efficiency of extraction with higher absorbance and D. values .

As well as from the slope of straight lines Fig(8) is appear there is one molecule of TBP or MIBK participated in the structure of complex extracted to the organic phase.

$[Co(PAN)^{-}(TBP)]^{+}; Cl^{-}$, $[Co\ (PAN)^{-}(MIBK)]^{+}; Cl^{-}$

$[Co^{+2}(PAN)^{-}\ (Cl^{-})(TBP)]$, $[Co^{+2}\ (PAN)^{-}(Cl^{-})(MIBK)]$

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