



CLOUD POINT EXTRACTION METHODOLOGY FOR SEPARATION AND DETERMINATION LEAD (II) BY USE NEW AZO-DERIVATIVE

Dr. Shawket K. Jawad* & Luay A. Khaleel**

Department of Chemistry, College of Education, Iraq

Abstract:

Extracted lead (II) as chloro anion $PbCl_4^{2-}$ by used laboratory synthesized new azo derivative 4-[anti pyrine azo]-p-benzennaphthol [APABN] after formation ion pair association complex in presence 0.5M HCl via cloud point extraction method by used nonionic surfactant 1%TritonX-100. The ion pair complex extracted has maximum absorbance at $\lambda_{max} = 470nm$, CPE method needed for separation heating in electrostatic water bath at 85 °C for 15 minutes, with studied all optimum conditions as well as effective factors such as electrolytes and interferences so that stoichiometry show the ion pair complex extracted was 1:1 $[H-APABN]^+$; $HPbCl_4^-$ or $[2H-APABN]^{+2}$; $PbCl_4^{2-}$ as well as thermodynamic study show $\Delta H_{ex} = 0.1703 \text{ KJ mol}^{-1}$, $\Delta G_{ex} = -64.467 \text{ KJ mol}^{-1}$, $\Delta S_{ex} = 180.55 \text{ J mol}^{-1} \text{ K}^{-1}$.

Key Words: Lead (II), Cloud Point Extraction & Liquid Ion Exchange

Introduction:

Whereas cloud point extraction methodology consider as sensitive method therefore to received widespread applications one of this applications extraction of Mg^{+2} ion as $Mg(NO_3)_2$ according to solvation method with 0.5M KNO_3 by use non ionic surfactant 1%TritonX-100 and 2,4-dimethyl-3-pentanone [1] selenium in kany kony (ipomoeareptans P) extracted and determined by cloud point extraction methodology by use of nonionic surfactant 1%TritonX-100 and Dithizone [2] by used CPE methodology with new laboratory prepared and nonionic surfactant 1%TritonX-100 extracted and determined Zn(II) [3], Many application of CPE method with different agent used for separation and determination metal ions with specific method for each ion [4-8]. Distribution ion pair association complex according to CPE method based for separation and determination metal ion [9-11].

Experimental:

1. Apparatus:

For UV-Vis spectrophotometric studies as well as for absorbance measurement used Biochrom spectrophotometer (80-7000-11) Libra 560 Cambridge CB40FJ, and for IR. Spectrophotometric used Legeunicamsp³-2001 Infrared spectrophotometers, as well as used electrostatic water bath (WNB7-45 England) for maintain temperature.

2. Materials and Solution:

All chemicals imported from trust worthy commercial company and used as received without more purification stock solution of lead(II) 1mg/ml prepared by dissolved 0.1598gm of $Pb(NO_3)_2$ (after dried at 110°C in oven) in 100ml distilled water by used volumetric flask. Other working solutions prepared by dilution with distilled water in suitable volumetric flask, as well as all other solution need in this Research prepared at the same procedure.

3. Principal Method:

10ml aqueous solution contain fixed quantity of Pb^{2+} ion and optimum concentration HCl with $1 \times 10^{-4} \text{ M}$ [APABN] with 0.5ml of 1%TritonX-100, heating this solution for optimum temperature and time until formation cloud point layer CPL with smaller volume and higher density separate this layer and dissolved in 5ml ethanol, then measure the absorbance of alcoholic solution at λ_{max} ion pair complex extracted

against blank prepared at the same manner without Pb^{2+} ion, and aqueous solution treated according to spectrophotometric method (Dithizone method) [12] and return to calibration curve Fig(1) to determine remainder quantity of Pb^{2+} ion in aqueous solution after extraction, subtraction this quantity from origin quantity Pb^{2+} ion in aqueous solution to determine transfer quantity into CPL as ion pair association complex, afterward calculate Distribution ration.

$$D = \frac{[Pb^{2+}]_{CPL}}{[Pb^{2+}]_{aq}}$$

Results and Discussion:

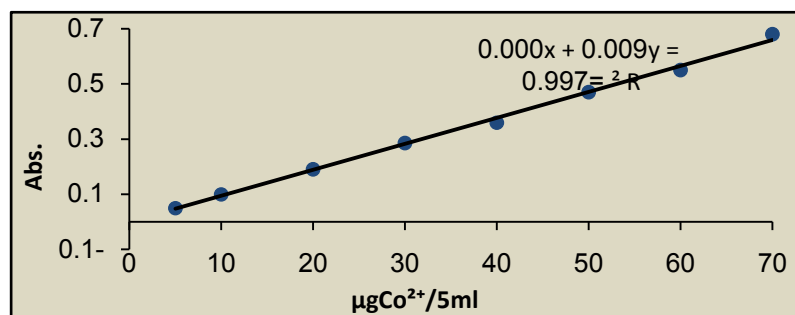


Figure (1): Calibration curve for determination remainder Pb^{2+} ion in aqueous solution (Dithizone method)

Spectrophotometric Studies:

For situation structure of laboratory prepared azo derivative 4-(anti pyrine azo)-P-benzen naphthol taken UV-visible spectrum and IR spectrum as in figures (2, 3) which in advocated structure suggested.

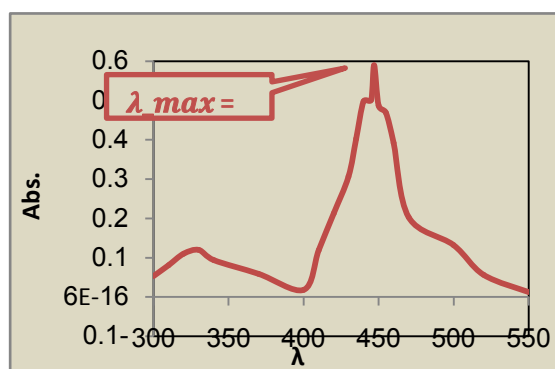


Figure (2): UV-Vis absorption spectrum for APABN

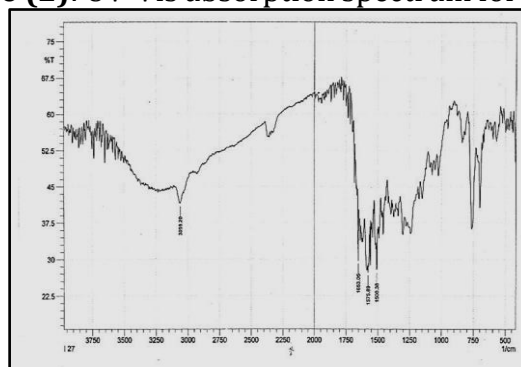


Figure (3): IR – spectrum for APABN

10mlaqueous solution contain 50µg Pb^{2+} ion, 0.5M HCl, 1×10^{-4} M APABN and 0.5ml 1%TritonX -100 heating this solution at 85°C for 15 minute in electrostatic water bath

until formation CPL which is separated and dissolved in 5ml ethanol, then taken UV-Vis spectrum for alcoholic solution against blank prepared at the same manner without Pb^{2+} ion the spectrum appear $\lambda_{max}=470nm$ as maximum absorbance wave length for ion pain complex extracted as in fig(4).

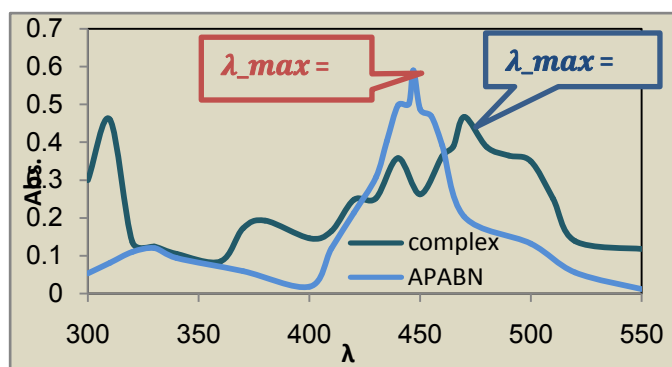


Figure (4): UV-Vis spectrum for ion pair association complex of Pb^{2+} ion with APABN
Variation HCl Concentration Effect:

Extracted Pb^{2+} ion from 10ml aqueous solution contain different concentration of HCl in presence 1×10^{-4} MAPABN and 0.5ml 1%TritonX-100 according to procedure detailed in principal method the results was as in Fig (5,6) .

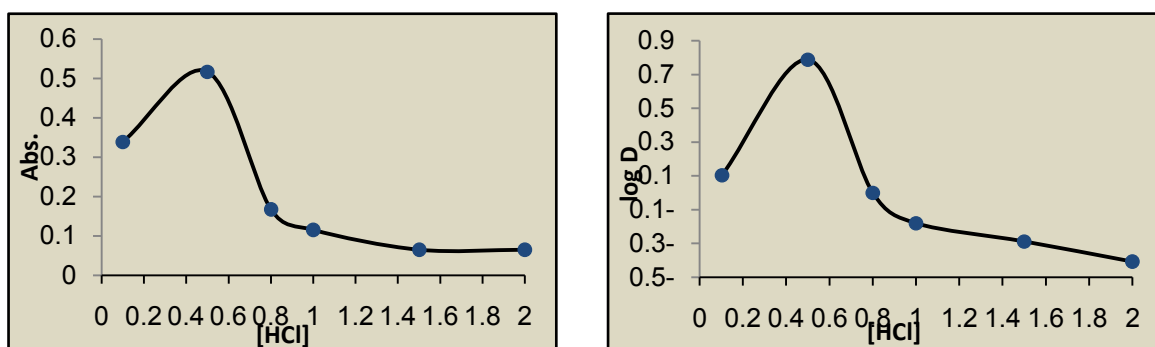
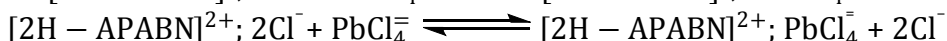
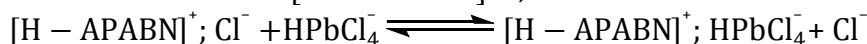
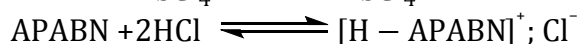
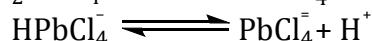
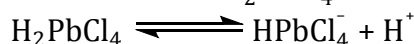
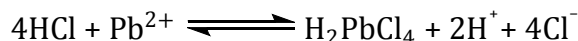


Figure (5): Effect of HCl concentration on ion pair

Figure (6): $D=F[HCl]$ complex formation and stability

The results show 0.5M HCl was the optimum concentration giving higher extraction efficiency because this concentration giving favorable thermodynamic equilibrium for formation chloro anion complex $PbCl_4^-$ as well as ion pair association complex.



Any concentration of HCl less than optimum not enough to reach thermodynamic equilibrium and effect to decrease extraction efficiency, so that concentrations more than optimum effect to decline extraction efficiency by region of formation stable compounds such as $PbCl_2$ or after oxidation $PbCl_4$ in addition to predominate

dissociation equilibrium $\text{PbCl}_4^{=}$ and ion pair complex according to mass action law and Le chatelier principle.

Variation Pb^{2+} Concentration Effect:

Extracted Pb^{2+} ion from 10ml aqueous solution contain different quantity of Pb^{2+} ion and 0.5M HCl, 1×10^{-4} M APABN and 0.5 ml of 1% Triton X-100 according to procedure detailed in principal method, the results as in fig(7,8).

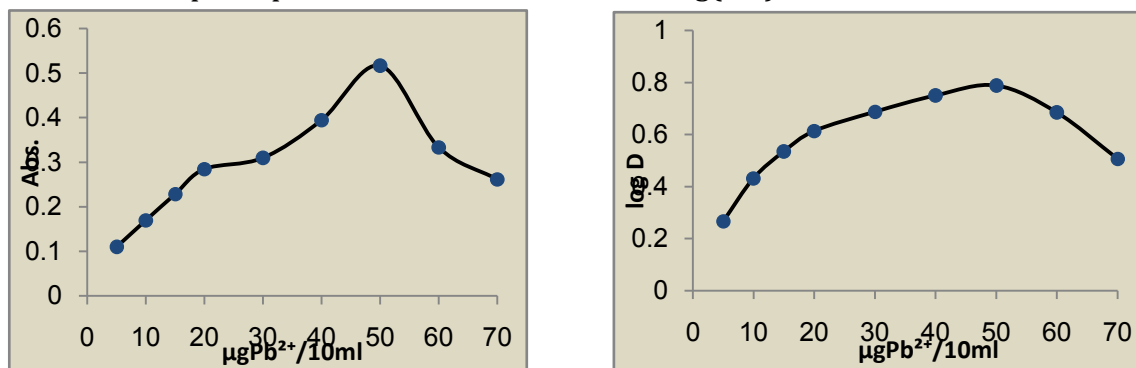


Figure (7): Effect of Pb^{2+} concentration on ion pair efficiency and D value

Figure (8): Effect of Pb^{2+} concentration on extraction complex formation and stability

The results show 50 μg was the optimum concentration of Pb^{2+} ion at constant other factors which is permit to reach best thermodynamic equilibrium and decline extraction efficiency as well as any concentration more than optimum value decrease extraction efficiency also by effect of mass action law and Le chatelier principle.

Variation Extractant Concentration Effect:

Extracted Pb^{2+} ion according to procedure detailed in the principal method at optimum conditions except using different concentrations of APABN the results was as in fig (9, 10).

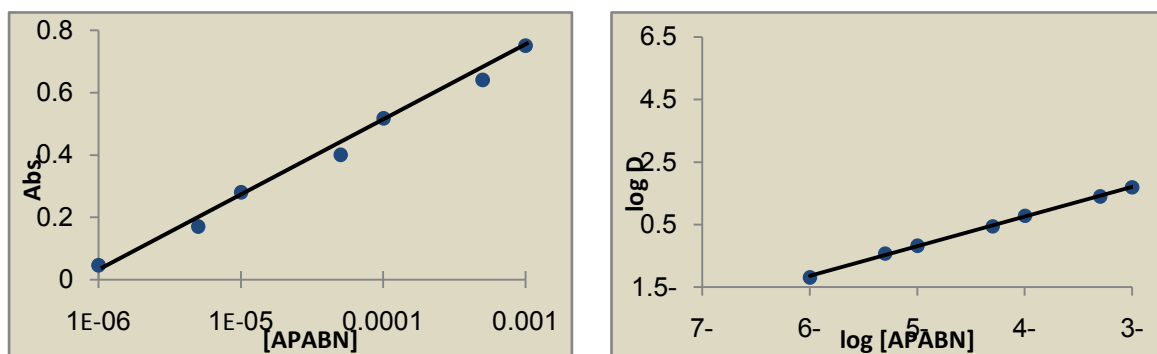


Figure (8): Effect of APABN concentration on complex formation

Figure (9): Effect of APABN concentration on extraction efficiency

The results show there is linear relation between absorbance and molar concentration of extractant APABN that is mean increase formation of ion pain complex with increase concentration of APABN.

Effect of Surfactant Volume:

Extracted 50 μgPb^{2+} ion in 10ml aqueous solutions in presence 0.5M HCl, 1×10^{-4} M APABN and different volume of 1% TritonX-100 according to procedure detailed in the principal method the results was as in fig(11, 12).

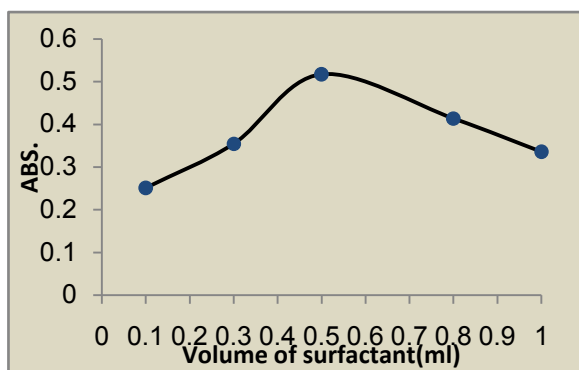


Figure (11): Effect of surfactant volume on ion pair transfer and absorbance

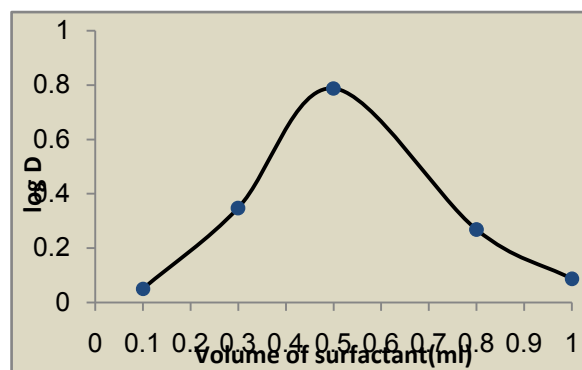


Figure (12): Effect of surfactant volume extraction efficiency and D-value

The results show 0.5ml of 1% TritonX-100 was the suitable to formation cloud point layer at the state of CMC which is mean giving best thermodynamic and kinetic equilibrium to aggregation micelles to form CPL with higher density and smaller volume to be best layer for transfer ion pair association complex and giving higher extraction efficiency, any volume less than optimum not permit to reached equilibrium of formation CPL, and decline extraction efficiency volume of surfactant more than optimum value effect to increase diffusion of micelles and decrease aggregation of micelles as well as decrease extraction efficiency.

Temperature Effect:

Extracted 50µg Pb²⁺ ion in 10ml aqueous solution contain 0.5MCl, 1x10⁻⁴ M APABN 0.5ml 1% TritonX-100 heated there solution in electrostatic water bath for different temperature and for 15 minutes at each temperature and complete the procedure as detailed in principal method, the results was as in fig(13,14).

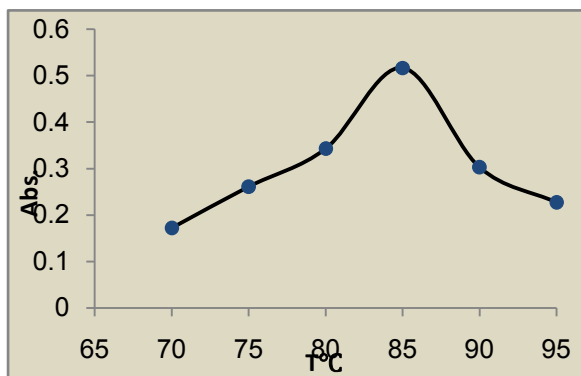


Figure (13): Effect of temperature on ion CPL formation and complex transfer

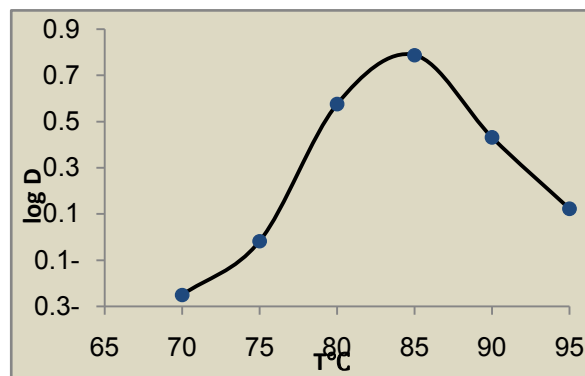


Figure (14): D=F(T°C)

The results show 85°C was the optimum temperature for formation CPL with higher dehydration to appear higher extraction efficiency. After calculate extraction constant K_{ex} at each temperature from the relation below.

$$K_{ex} = \frac{D}{[Pb^{2+}][APABN]}$$

Afterward plot log K_{ex} against 1/T K as in fig (15).

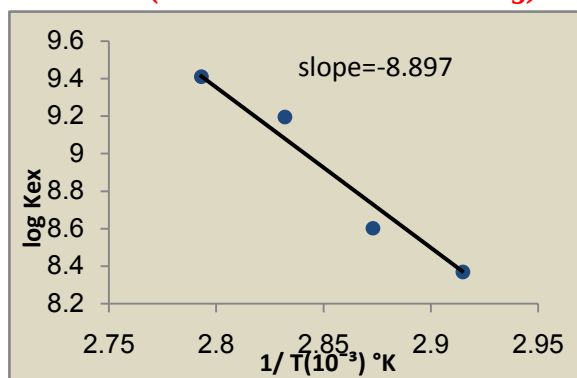


Figure (15): Effect of temperature on K_{ex} values from the slope of this straight line and thermodynamic relations

$$\text{slope} = \frac{-\Delta H_{ex}}{2.303 R} \Delta G_{ex} = -RT \ln K_{ex} \Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$$

ΔH_{ex}	ΔG_{ex}	ΔS_{ex}
0.1703 KJ.mol ⁻¹	-64.467 KJ.mol ⁻¹	180.55 J.mol ⁻¹ K ⁻¹

Effect of Heating Time:

According to principal method extracted Pb^{2+} ion from 10ml aqueous solution at optimum conditions except heating for different time results was as in fig (16,17) .

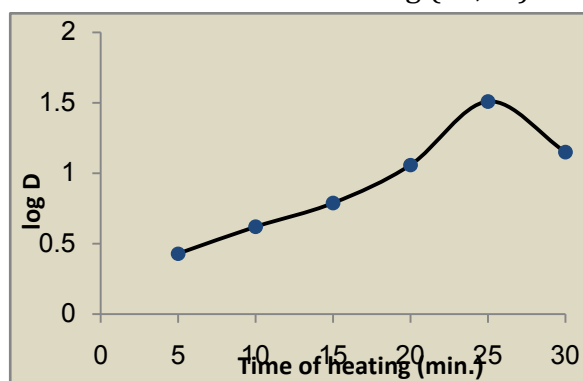
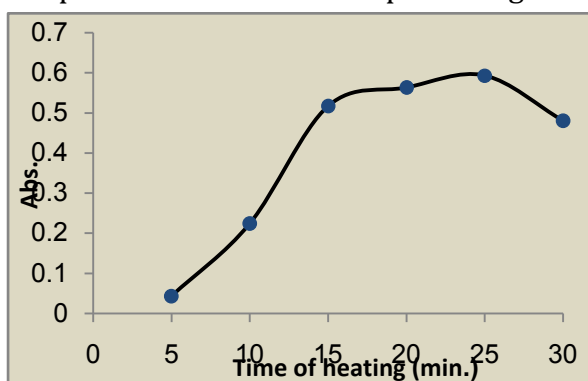


Figure (16): Effect of heating time on formation CPL efficiency and D-values

Figure (17): Effect of heating time on extraction

The results show 25minutes was the optimum heating time giving higher absorbance and D-value, because the quantity of heat at this temperature was the favorable for kinetic equilibrium to formation CPL with higher density and smaller volume. Any time less than optimum not allow reaching kinetic equilibrium for aggregation micelles, but the time more than optimum value giving increasing in kinetic energy which is effect to increase diffusion of micelles.

Stoichiometry:

For demonstrate the more probable structure of ion pair association complex extracted into cloud point layer by following two spectrophotometric methods slope analysis method and slope ration method . According to procedure detailed in the principal method. The result was as in fig (18, 20).

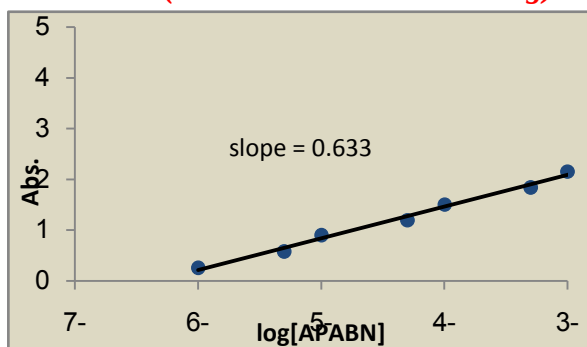


Figure (18): slope analyses method

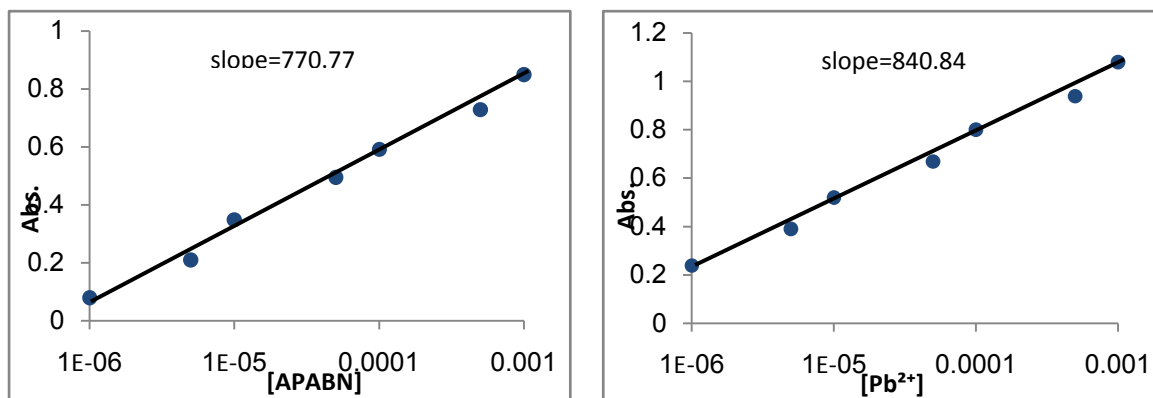
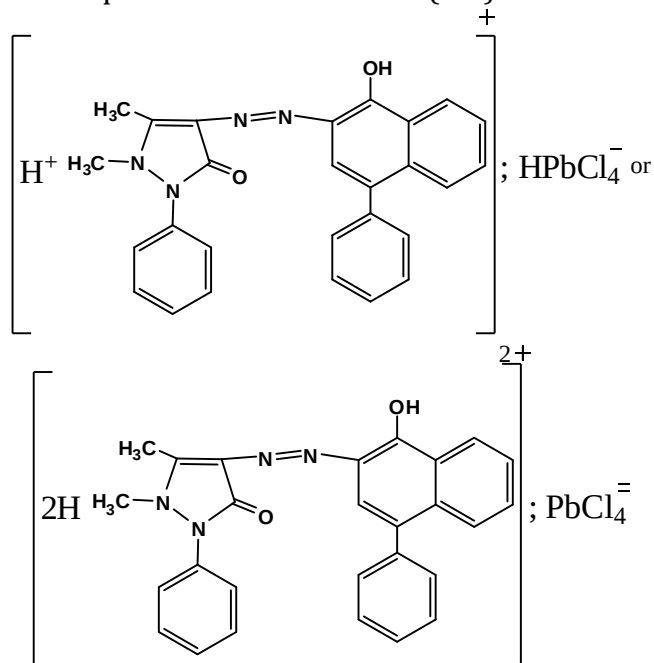


Figure (19): Effect of APABN concentration on extraction efficiency

Figure (20): Effect of Pb^{2+} concentration on ion complex formation

Slope ratio = 0.917

From this method the mire probable structure was (1:1).



Effect of Electrolytes:

Extracted Pb^{2+} ion from 10ml aqueous solution at optimum conditions in presence 0.1M some electrolyte salts according to principal method, the results was as in Table(1).

Table (1): Effect of electrolyte salts

Electrolyte	Abs	D
LiCl	0.827	332.3
NaCl	0.724	249.00
KCl	0.687	141.86
NH ₄	0.609	70.43
MgCl ₂	0.763	99.00
CaCl ₂	0.679	82.33
AlCl ₃	0.739	61.50

The results show presence electrolyte in aqueous solution effect to increase extraction efficiency by reason of increase dehydration and stability of CPL in addition to increase destroy the hydration shell of metal ion to increase probable of complexation.

Effect of Interferences:

Extraction Pb²⁺ ion from aqueous solution according to principal method at optimum conditions and in presence of 0.1M for some metal ions, the results was as in Table (2).

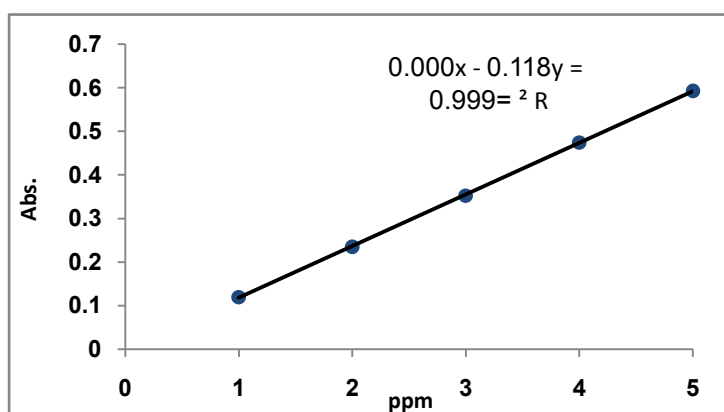
Table (2): Effect of interferences on extraction efficiency

Interferences	Abs	D
Cd ²⁺	0.466	14.27
Ni ²⁺	0.403	9.64
Hg ²⁺	0.554	22.43
Cr ₂ O ₇ ⁼	0.487	18.51

The results show the cations and anion Cr₂O₇⁼ giving interfere with Pb²⁺ and effect to decline extraction efficiency for Pb²⁺ ion in spite of there is not at optimum condition for each ion interfere.

Spectrophotometric Determination of Pb²⁺ ion:

For determination Pb(II) in different samples by application cloud point method for separation to determine spectrophotometrically prepared calibration curve according to the principal method under optimum condition such as fig (21).



RSD %	$\epsilon \text{L.mol}^{-1}.\text{cm}^{-1}$	D.L ppm	S $\mu\text{g}/\text{cm}^2$
0.0052	245739.2	2.289×10^{-6}	2.398×10^{-10}

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