Extraction of Silver (I) from Aqueous Solutions by 2-[(4-Chloro-2-Methoxy phenyl) azo]-4,5-diphenyl imidazole

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الخلاصة

طرق الاستخلاص لأيونات الفضة (I) من المحاليل المائية بواسطة الليگاند 2-[(4-Chloro-2-Methoxy phenyl) azo]-4,5-diphenyl imidazole (4-ClMePADPI) بينت إن المحاليل المائية يجب أن تكون قيمة الدالة الحامضية لها (pH=10) ،وإن تركيز ايونات الفضة Ag^+ هو (40 µg)(7.36×10^{-5}M) ،وزمن رج مقداره (10 دقيقة)، دراسة تأثير المذيبات العضوية على عملية الاستخلاص أوضحت انه لا توجد علاقة خطية بين قيم ثوابت العزل الكهربائي (ε) للمذيبات العضوية المستعملة وقيم نسب التوزيع (D)لعمليات الاستخلاص وأوضحت النتائج إن هناك تأثير لتركيب المذيب العضوي على عملية الاستخلاص، أما دراسة تركيب معقد الترابط الأيوني المستخلص بينت إن المعقد هو (١:١) (فلز:ليگاند) $[Ag(4\text{-ClMePADPI})]^+NO_3^-$ الدراسة الثرموديناميكية أوضحت إن التفاعل بين ايونات الفضة Ag^+ و الليگاند (4-ClMePADPI) كان تفاعل ماص للحرارة Endothermic reaction، كما إن دراسة تأثير الاشتراك Synergism لجزيئات TBP بينت إن جزيئة واحدة من TBP سوف تشترك في تركيب معقد الترابط الأيوني المستخلص-4)[Ag(ClMePADPI)(TBP)]$^+NO_3^-$.

Abstract

Extraction procedures for Ag^+ from aqueous solutions by 2-[(4-Chloro-2-Methoxy phenyl) azo]-4,5-diphenyl imidazole (4-ClMePADPI) shows aqueous solutions must be at (pH=10) and concentration of Ag^+ ions is (40µg)(7.36×10^{-5} M), with shaking time (١٠minutes), organic solvents effect on extraction method demonstrate there is not any linear relation between dielectric constant (ε) for organic solvents used and distribution ratio values (D), but there is effect for structure of organic solvent. Stoichiometry studies shows more probable structure of ion pair complex extracted was (1:1) (Metal:Ligand) $[Ag(4\text{-ClMePADPI})]^+NO_3^-$, temperature effect shows from thermodynamic viewpoint the reaction between Ag^+ ions and ligand (4-ClMePADPI) was endothermic reaction, synergism studies appear there is one molecules of TBP participate in ion pair complex extracted $[Ag(4\text{-ClMePADPI})(TBP)]^+NO_3^-$.

Introduction

High sensitivity and selectivity for azo compounds toward complexation with special transition metal elements giving attention about using these compounds for extraction, separation, spectrophotometric determination of transition elements, Luciene et al [1] used 4-(2-thiozolylazo)-resorcinol for spectrophotometric determination of Cr(III), giving red complex at pH=5.7 and slowly formation, and

using irradiating with microwave to accelerate the complex formation reaction. Sahar [2] used new derivative as ligand 2-(Benzothiazolyl azo)-4-benzyl phenol to prepare complexes with Co, Ni, Cu, Zn, Cd, Hg and studied structure and properties of these complexes. Ibrahim et al [3] synthesized new imidazole derivative and used as ligand as well studied it's complexes with Cobalt (II), Nickel (II) and Copper (II). Alaa [4] synthesized new ligand 2-(α-Naphthylazo)-4,5-diphenyl imidazole and used for extraction Cu^{2+}, Ag^{+} from aqueous solution and determine all conditions for extraction and the effective parameters on the extraction method. Ruijuan et al [5] synthesized chiral complexes of Zn(II) with imidazole derivatives and amino acid ester derivatives and studied characterization of these complexes. Maria atanassova [6] studied the solvent extraction of trivalent lanthanoids (La, Nd, Eu, Ho, Lu) with mixtures of the chelating extractants and 4-(2-pyridylazo)-resorcinol. Ibtihaj [7] synthesized new ligand 2-[4-carboxy methyl phenyl azo]-4,5-diphenyl imidazole and studied extraction of $Cu^{2+}$and Ag^{+} by this ligand and determined extraction conditions as well as all factors effect on extraction method. Mohamed et al [8] used 2-(2-benzimidazolyl azo)-4-acetamidophenol for extraction and preparation complexes with Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), at latter studied different properties of these complexes. Beniamin et al [9] studied the difference in the extraction process for Ni(II) and Zn(II) with two imidazole derivative ligand 1-Octylimidazole and 1-Octyl-2-Methylimidazole. Ibolya [10] studied Copper (II), Zinc (II) complexes of several imidazole containing ligands and some methylated derivatives of 1,3,5-trideoxy -1,3,5-tri amino cis-inositol ensuring rather rigid pre organized structures have been studied. Reginalodo et al [11] Iron and ruthenium complexes with benzothriazole and benzimidazole derivatives were prepared and characterized in aqueous solution by means of electrochemical and spectroelectrochemical methods.

Experimental

Absorption and spectrophotometric measurements were made using a single beam UV-Visible spectrophotometer (schimadzu UV-100-02) and double beam (UV-1700) UV-Visible spectrophotometer schimadzu, pH measurements were carried out using (Aschott-Gerate) pH-meter Model 820.

All reagents and solvents were obtained from commerical sources and used as received, as well all solutions prepared by use volumetric flask. Stock solution of Ag^{+} (1mg/ml) prepared by dissolved (1.575 gm) of $AgNO_3$ dryer at (110°C) in distilled water contain (1ml) of concentrated nitric acid and diluted to 1 Liter, other working solutions prepared by dilution with distilled water, stock solution of dithizone needful to determination of Ag^{+} ions in aqueous solution at concentration (1×10^{-2}M) prepared by dissolved (0.0256 gm) in (10ml) of carbon tetra chloride CCl_4 in volumetric flask, other working solutions prepared by dilution with CCl_4, stock solution of ligand (4-ClMePADPI) at concentration (1×10^{-2}M) prepared by dissolved (0.0366gm) in (10ml) of chloroform, other working solutions prepared by dilution with chloroform.

General experiments to rely on taken (5ml) aqueous phase contain fixed quantity from Ag^+ at optimum pH and added (5ml) organic solution for ligand (4-ClMePADPI) dissolved in chloroform at (1×10^{-4}M) concentration, after shaking the two solution for optimum shaking time separate the two layers and determine the remaining Ag^+ ions in aqueous solution by spectrophotometric method (dithizone method) [12]. After determine transfere quantity of Ag^+ ions to the organic phase to form complex and calculate distribution ratio (D).

Results and Discussion

Effect of Ph

Extracted (20µg) Ag^+ ions (3.68×10^{-5} M) in (5ml) aqueous solutions at different pH values (5-11) by (5ml) ligand solution (4-ClMePADPI) dissolved in chloroform at (1×10^{-4}M) concentration, after shaking for 10 minutes and separate organic phase from aqueous phase, determine the remaining quantity of Ag^+ ions in aqueous phase according to spectrophotometric method [12], from the absorbance values and calibration curve Figure (1) determine quantity of Ag^+ ions in aqueous phase, latter calculate distribution ratio (D), after plot log D versus pH provide the Figure (2) demonstrate the optimum pH value which is giving higher value for distribution ratio (D) was (pH_{ex}=10).

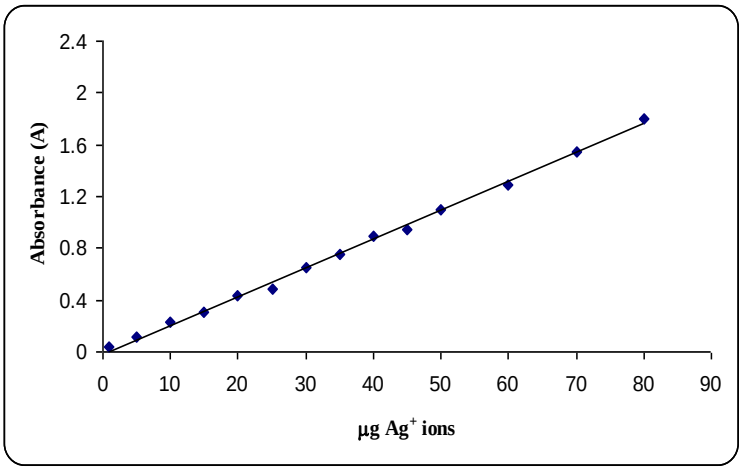

Figure 1: Calibration curve for Ag^+ ions

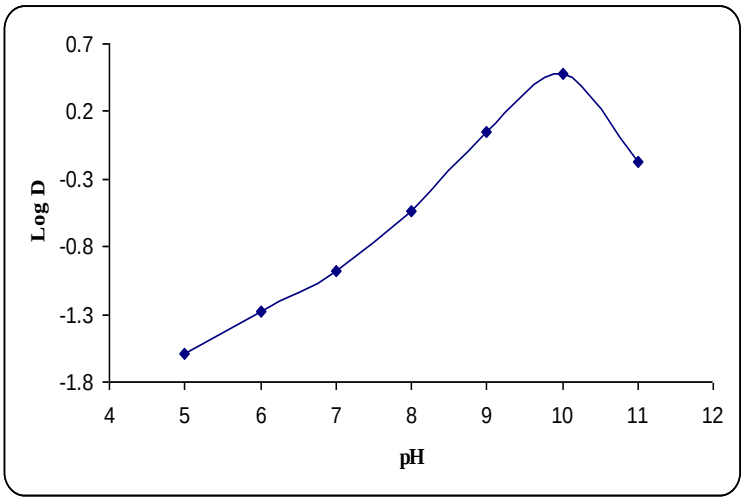

Figure 2: Effect of pH on extraction of Ag^+ ions

Effect of Metal Ion Concentration

Extracted Ag^+ ions from (5ml) aqueous solutions contain different quantity (5-80 µg) (9.2×10^{-3} - 1.47×10^{-4}M) at (pH=10) by (5ml) ligand solution (4-ClMePADPI) dissolved in chloroform at (1×10^{-4}M) concentration, after shaking for 10 minutes separate layers from each others, determine remaining quantity of Ag^+ ions in aqueous phase by spectrophotometric method [12]. Latter calculate distribution ratio (D) at each concentration of Ag^+ ions, after that graph log D values versus µg Ag^+ ions provide Figure (3).

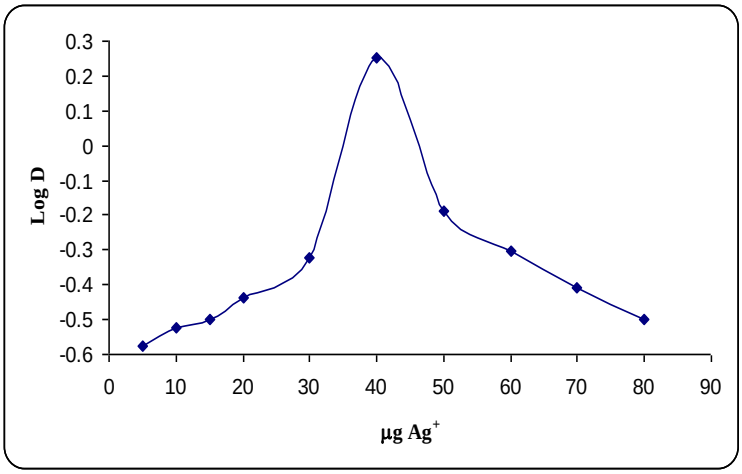

Figure 3: Effect of metal ion concentration on distribution ratio (D)

Results show optimum concentration giving higher distribution ratio (D) was (40µg) Ag^+ ions (7.36×10^{-5} M), who represent suitable concentration for complexation reaction to produce stable ion pair complex extracted, less this concentration not able to realization equilibrium, as well as high concentration predomenate dissociation equilibria.

Effect of Shaking Time

Extracted (40µg) Ag^+ ions (7.36×10^{-5} M) in (5ml) aqueous solutions at (pH=10) by (5ml) ligand solution (4-ClMePADPI) dissolved in chloroform by shaking the two layers for different time (5-25minutes), after calculate distribution ratio (D) at each shaking time according to spectrophotometric methods [12], and plot log D values against shaking time provide Figure (4).

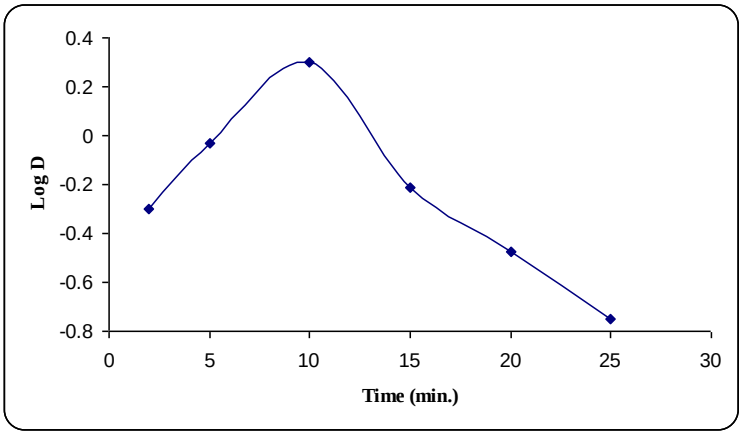

Figure 4: Effect of shaking time on distribution ratio (D)

Results shows optimum shaking time, which is necessary to reach the equilibrium, was (10min.).

Effect of Organic Solvents

Extracted (40µg) Ag^+ ions (7.36×10^{-5} M) in (5ml) aqueous solution at (pH=10) by (5ml) ligand solution (4-ClMePADPI) dissolved in different organic solvents differ in dielectric constant (ε) at (1×10^{-4}M) concentration. After shaking for optimum shaking time determine remaining Ag^+ ions in aqueous solution and distribution ratio (D) by spectrophotometric method [12], get the results at Table (1), shows there is not any linear relation between distribution ratio (D) and dielectric constant (ε), but there is effect for organic solvent structure to participate in the structure of ion pair complex extracted as contact ion pair or loose ion pair.

Table 1: Effect of organic solvents on distribution ratio (D)

Organic solvents	ε	D
Dichloromethane	9.08	1.76
Chloroform	5.708	2.00
Bromo benzene	5.40	1.86
Benzene	2.804	0.538
Toluene	2.438	0.633
Carbon tetrachloride	2.38	0.51

Stereochemistry

-Slope Analysis Method

Extracted (40µg) Ag^+ ions (7.36×10^{-5}M) in (5ml) aqueous solutions at (pH=10) by (5ml) ligand solution (4-ClMePADPI) dissolved in chloroform at different concentration (1×10^{-6} - 1×10^{-2}M), after determine spectrophotometricaly distribution ratio (D) at each concentration of ligand, latter graph log D versus log [4-ClMePADPI] giving straight line Figure (5) with slope (0.22) demonstrate more probable structure of ion pair complex extracted was (1:1) (metal :ligand) $[Ag(4\text{-}ClMePADPI)]^+NO_3^-$.

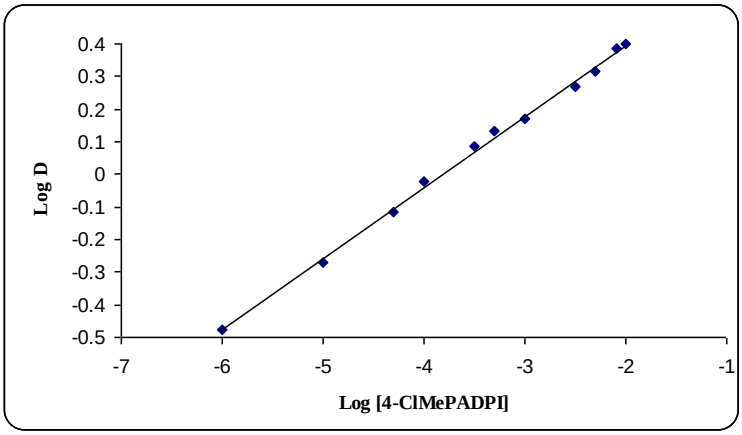

Figure 5: Slope analysis method

Mole Ratio Method

Extracted (40µg) Ag^+ ions (7.36×10^{-5}M) in (5ml) aqueous solutions at (pH=10) by (5ml) ligand solution (4-ClMePADPI) dissolved in chloroform at different concentration (1×10^{-6}-1×10^{-2}M), after shaking for optimum shaking time separate the two layers, latter determine the absorbance of organic phase at λ_{max}=519nm, and plote absorbance (A) values versus C_L/C_M as in Figure (6), shows the structure of ion pair complex extracted was (1:1) (metal :ligand) $[Ag(4\text{-ClMePADPI})]^+NO_3^-$.

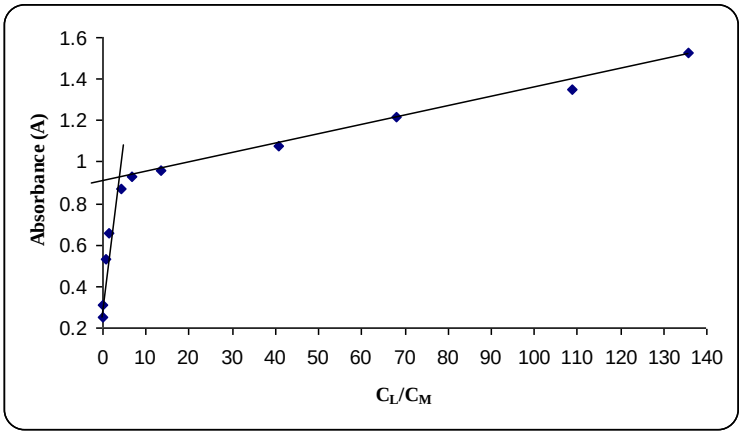

Figure (6): Mole ratio method

Continuous Variation Method

Prepared aqueous solution for Ag^+ ions and ligand solution (4-ClMePADPI) dissolved in chloroform both at (1×10^{-4}M) concentration and mixed different volume of each solution to (5ml) volume of mixture at (pH=10) after shaking for optimum shaking time separate the two layer determine absorbance of organic phase at λ_{max}=519nm, latter plote absorbance versus (V_M/V_T) as in Figure (7),the results confirm the structure of ion pair complex extracted was (1:1) (metal :ligand) $[Ag(4\text{-ClMePADPI})]^+NO_3^-$.

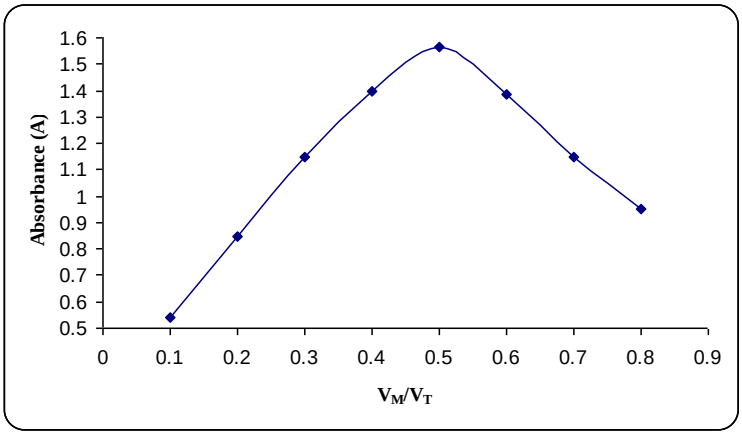

Figure 7: Continuous variation method

Temperature Effect

Extracted (40µg) Ag^+ (7.36×10^{-5}M) in (5ml) aqueous solutions at (pH =10) by (5ml) of ligand solution (4-ClMePADPI) dissolved in chloroform at (1×10^{-4}M) concentration at different temperature (5°C-60°C), after shaking for optimum shaking time and separated the two layers, determine spectrophotometricaly [12] of Ag^+ ions remaining in aqueous solution, latter calculate distribution ratio (D) at each temperature, proceed the results at Table (2), according to relation below. Calculate extraction constant K_{ex}, and from the slope value of straight line relation between log K_{ex} versus 1/T °K determine thermodynamic data of reaction between ligand with Ag^+ ions:

$$K_{ex}= \frac{D}{[Ag^+]_{aq.}\,[4\text{-ClMePADPI}]_{org.}}$$

$$\text{Slope} = \frac{-\Delta H_{ex}}{2.303R}$$

$$G_{ex}=-RT\ln (K_{ex})$$

$$\Delta G_{ex}= \Delta H_{ex}-T\,\Delta S_{ex}$$

Table 2: Effect of temperature on extraction of Ag^+ ions

T °C	1/T °K $\times10^{-3}$	D	$K_{ex}\times10^{8}$	ΔH_{ex} KJ mole^{-1}	ΔG_{ex} KJmole^{-1}	ΔS_{ex} J mole $^{-1}$K^{-1}
5	3.6	0.54	0.073	0.0324	-55.36	166.34
10	3.5	0.87	0.117			
15	3.47	1.00	0.135			
20	3.4	1.26	0.170			
30	3.3	2.00	0.270			
40	3.2	2.63	0.355			
50	3.1	3.55	0.479			
60	3.0	5.62	0.758			

The results show the reaction between ligand (4-ClMePADPI) with Ag^+ ions was endothermic.

Synergism Effect

Extracted (40µg) Ag^+ ions (7.36×10^{-5}M) in (5ml) aqueous solutions at (pH =10) by (5ml) ligand solution (4-ClMePADPI) dissolved chloroform at (1×10^{-4}M) concentration contain different concentration of tributylphosphate (TBP)(1×10^{-6}-1×10^{-7}M) after shaking the two layer for optimum shaking time, determine distribution ratio (D) at each concentration of TBP, latter graph of log D versus log [TBP], giving straight line Figures (9) which slope equal to (0.071) demonstrate ion pair complex extracted contain one molecules of TBP which is effect to enhancement in distribution ratio value by replacement water molecule binding to coordination shell of metal ion Ag^+ and increase partition to organic phase $[Ag(4\text{-}ClMePADPI)]^+NO_3^-$.

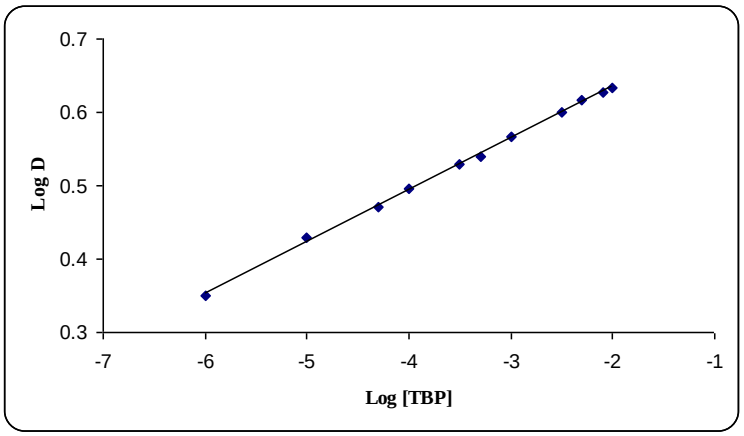

Figure 9: Synergism effect

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