

Complexation and Extraction Studies of 2-[(Benzothiazolyl) azo]-4-benzylphenol with Cd⁺² Ion

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Abstract

The extraction method shows optimum pH of extraction was (pHex= 9), and the reaction of complexation need 50µg Cd⁺² ion (8.89×10⁻⁵M) in aqueous solution to give higher distribution ratio and more stable complex, shaking time necessary to reach equilibrium was (10minutes), as well as stoichiometry studies show the more probable structure of complex extracted was (1:1) (Metal:Ligand) [Cd⁺²(BTABP)(Cl⁻)], organic solvent effect was study demonstrate there is no linear relation between dielectric constant (ε) of organic solvent and distribution ratio (D), but there is an effect for organic solvent structure to participate in the formation of complex, effect of temperature on extraction method shows that reaction between ligand (BTABP) and Cd⁺² ion was endothermic reaction and the enthalpy of extraction ΔHex = 0.0087 KJ.mol⁻¹ Gibb, Free energy ΔGex = 52.4 KJ.mol⁻¹ and entropy ΔSex= 157.4 KJ.mol⁻¹, synergism effect shows participate one molecule of TBP in each molecule of complex formed and effect to enhanced distribution ratio (D) [Cd⁺²(BTABP)(Cl⁻)(TBP)].

الخلاصة

دراسة الاستخلاص بينت ان قيمة الدالة الحامضية المثلى للاستخلاص كانت (pHex= 9) وان تفاعل التعقيد يحتاج إلى 50µg من ايونات الكاديوم (8.89×10⁻⁵ M) في المحلول المائي ليعطي أعلى قيمة لنسبة التوزيع (D) ومعقد أكثر استقراراً. زمن الرج اللازم للوصول إلى حالة التوازن كانت (10 دقائق) وكذلك دراسة تركيب المعقد أوضحت ان تركيب المعقد الأكثر احتمالاً المستخلص كان (1:1) (فلز:ليكاند) [Cd⁺²(BTABP)(Cl⁻)]. دراسة تأثير المذيب العضوي بينت انه لا توجد علاقة خطية بين ثابت العزل الكهربائي (ε) وقيم نسب التوزيع (D) ولكن هناك تأثير لتركيب المذيب ومشاركة المذيب العضوي في تكوين المعقد، أما تأثير درجة الحرارة على عملية الاستخلاص فقد أوضحت الدراسة ان التفاعل بين الليكاند (BTABP) وايونات الكاديوم Cd⁺² كان التفاعل ماص للحرارة Endothermic وان انثالي الاستخلاص كان ΔHex=0.0087 KJmole⁻¹ وان الطاقة الحرة للاستخلاص كانت ΔGex = -52.4 KJ mole⁻¹ أما قيمة انتروبي للاستخلاص ΔSex= 157.4 Jk-1mole⁻¹ أما تأثير المشاركة Synergism فقد بينت الدراسة ان هناك جزيئة واحدة من TBP تشترك في تركيب المعقد المستخلص والتي تسبب في ارتفاع قيم نسب التوزيع (D) [Cd⁺²(BTABP)(Cl⁻)(TBP)].

Introduction

Dependence on selectivity and sensitivity of azo compound for spectrophotometric determination and extraction of transition metal cations, Mohamed et al. (2001) prepared a new ligand 2-[2-benzimidazolylazo]-4-acetamidophenol and its complex with Fe (III), Co (II), Ni (II), Cu (II), Zn (II) and Cd (II)[1].Beniamin et al. studies the comparison of extraction Zn (II) and Ni

(II) complexes by use 1-Octylimidazole and 1-Octyl-4 methylimidazole[2]. Lucienes et al. used 4-(2-thiazolylazo)-resorcinol (TAR) for spectrophotometric determination of chromium in steel [3]. Ibrahim et al. (2006) prepared a new imidazole ligand benzo (15-crown-5)-14 imidazole [4, 5, f] phenanthroline and studied the characterization of its complex, with Co (II), Ni (II) and Cu (II)[4]. SAN and Chlittaran (2001) study the reactivity of cis RuCl₂ fragments in Ru(pph₃)₂ (TaiMe)Cl₂ with N,N-Chelators (TaiM=1-methyl-2-(p-tolylazo)imidazole)[5]. Ibtihaj (2005) synthesized a new imidazole ligand 2-[(4-Carboxymethylphenyl)azo]-4,5-diphenyl imidazole and studied the extraction of Cu (II) and Ag (I) by solvent extraction method[6]. Alaa (2006) synthesized a new imidazole ligand 2-[α -Naphthylazo]-4,5-diphenyl imidazole and studied the extraction of Cu (II) and Ag (I) by this ligand according to solvent method[7]. REDDY et al. (2003) used Benzildithiosemicarbazone (BDTSC) as sensitive and selective analytical reagent for the extractive spectrophotometric determination of copper (II), this reagent react with Cu (II) in which is the range of pH 1-7 to formed yellowish complex[8], Ruijnen et al. (2006) synthesized A chiral complex salen Zn (II) and studied characterized coordination with imidazole derivatives by uv-vis. Spectrophotometric titration and CD spectroscopy[9]. Zainab (2006) synthesized a new imidazole ligand 2-[(4-Chloro-2-methoxyphenyl)azo]-4,5-diphenyl imidazole and studied complexation and extraction of Zn (II), Cd (II) and Hg (II)[10]. Won et al. (2002) synthesized a new polystyrene divinyl benzene resin containing 2-(2-Thiazolylazo)-5-dimethyl aminophenol (TAM) functional groups has studied its sorption behavior for nineteen metal ions, including Zr (IV), Hf (V), V (VI) and investigated by batch and column method[11], Maria (2006) studied the solvent extraction of trivalent lanthanides (La, Nd, Eu, Ho, Lu) with mixture of the chelating extractant 1-(2-Thienyl)-4,4,4-trifluoro-1,3-butane dionethenoyl trifluoro acetone (HTTA) or 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5- or (HP) and 4-(2-pyridylazo)-resorcin (PAR) in CHCl₃ was studied[12].

2. Experimental

2.1. Apparatus and standard solutions

Shimadzu (UV-100-02) spectrophotometer single beam and (UV-1200) double beam spectrophotometer, Japan used for all absorption and spectrum measurement, for pH measurement, used (HANNA pH-meter).

All reagents and solvents were obtained from commercial sources and used as received. The ligand 2-[Benzothiazolylazo]-4-benzylphenol (BTABP) synthesized as in the thesis[13], (1mg/ml) solution of Cd⁺² ion was prepared by dissolving (0.1631gm) of CdCl₂ dried at (110°C) in water contain (2ml) of conc. HCl and dilute the solution to (100ml) by distilled water in volumetric flask, all other working solutions of Cd⁺² ion are prepared by dilution with distilled water, ligand solution (1×10⁻²M) prepared by dissolving (0.345gm) in (100ml) of chloroform in volumetric flask, all other ligand solutions prepared by dilution with chloroform.

For spectrophotometric determination of Cd^{+2} ion in aqueous phase needful prepared ($1 \times 10^{-2}\text{M}$) stock solution of dithizone by dissolved (0.0256gm) in (10ml) of CCl_4 in volumetric flask, working solution ($1 \times 10^{-4}\text{M}$) prepared by dilution with CCl_4 .

2.2. General procedure

5 ml aqueous solution contain quantity of Cd^{+2} ion, shaking for suitable time with (5ml) of ligand (BTABP) dissolved in organic solvent at fixed concentration in optimum value of pH, at last separate aqueous phase from organic phase, afterward determine remainder quantity of Cd^{+2} ion in aqueous phase as well as transferred quantity by followed spectrophotometric determination method[14], after that calculate distribution ration (D).

3. Results and Discussion

3.1. Effect of pH on extraction methods

Extracted 30 μg Cd^{+2} ($5.34 \times 10^{-5}\text{M}$) in (5ml) aqueous phase at different pH (4-12) by 5 ml of ligand (BTABP) dissolved in chloroform at ($1 \times 10^{-4}\text{M}$), after shaking these two phases for (10 minutes) then separate these two layers and determined remainder quantity in aqueous phase and transferred quantity to the organic phase by followed procedure in [14], after that calculate the distribution ratio (D) as the result in Figure (1).

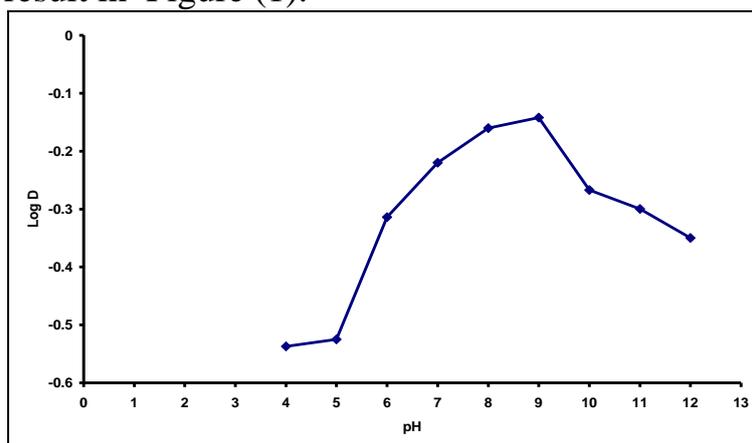


Figure (1): Effect of pH on the extraction of Cd^{+2} ions

The results in Figure (1) demonstrate the optimum pH for extraction was ($\text{pH}_{\text{Hex}} = 9$) which is giving higher value of distribution ratio (D).

3.2. Effect of metal ions concentration on extraction methods

Extracted Cd^{+2} ion from (5ml) aqueous phase contain different concentration of Cd^{+2} ion ($5\mu\text{g} - 80\mu\text{g}$) ($8.89 \times 10^{-6}\text{M} - 1.42 \times 10^{-4}\text{M}$) at ($\text{pH}_{\text{Hex}} = 9$) by (5ml) ligand (BTABP) dissolved in chloroform at ($1 \times 10^{-4}\text{M}$) after shaking these two layers for (10 minutes) separate organic phase from aqueous phase and determine Cd^{+2} ion in aqueous phase and organic phase by using the method in [14] and calculate distribution ratio (D) as in Figure (2).

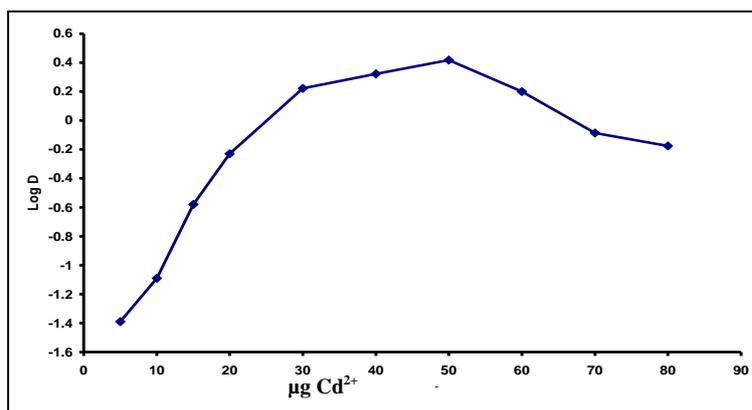


Figure (2): Effect of metal ion concentration on extraction method

Figure (2) illustrate 50µg Cd⁺² was the optimum concentration of metal ion which is giving higher distribution ratio (D).

3.3. Effect of Shaking Time

Extracted 50 µg Cd⁺² (8.89×10^{-5} M) in (5ml) aqueous solutions at (pHex= 9) with (5ml) of (1×10^{-4} M) ligand solution dissolved in chloroform at different shaking time after calculate distribution ratio (D) in each shaking time and plot log D against time of shaking in minutes the results giving the Figure (3) which is demonstrate the optimum shaking time was (10 minutes), and in this shaking time reached to the equilibrium of complexation reaction between ligand and Cd⁺² ion.

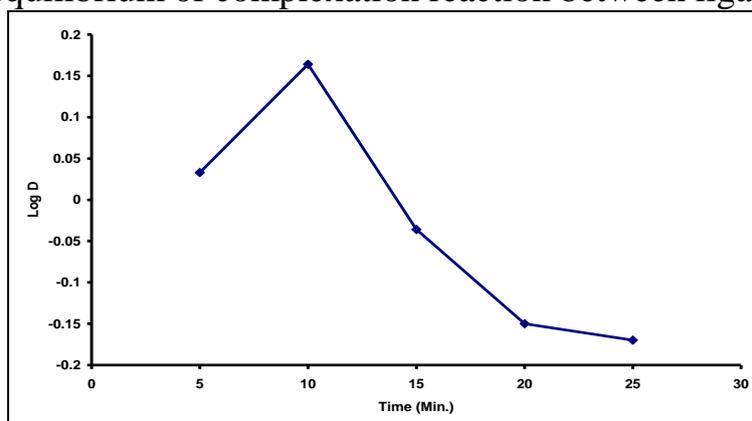


Figure (3): Effect of shaking time on extraction method

3.4 Stoichiometry

3.4.1 Slope analysis method

Extracted 50µg Cd⁺² (8.89×10^{-5} M) in 5 ml aqueous solutions at (pHex= 9) by (5ml) of ligand (BTABP) dissolved in chloroform at different concentrations (1×10^{-2} M – 1×10^{-6} M), after shaking each mixing for (10 minutes) and calculate distribution ratio (D) for each concentration of ligand, plot log D values against log [BTABP] to get Figure (4) from the slope of straight line shows that the structure of ion pairs complex extracted to organic phase was (1:1) (ligand:metal) [Cd⁺²(BTABP)(Cl⁻)].

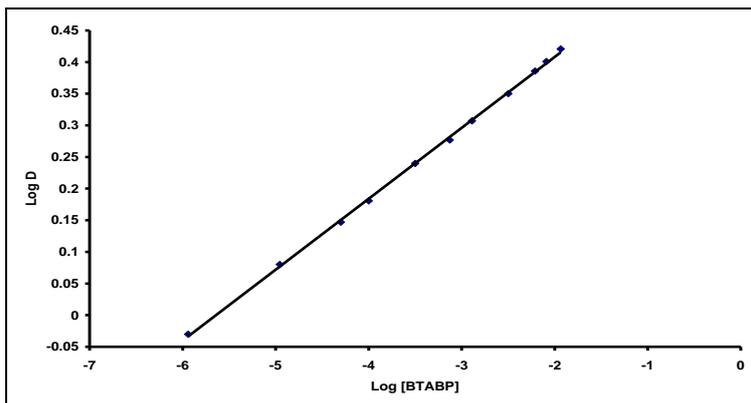


Figure (4): Slope analysis method for extraction Cd⁺² ions

3.4.2. Mole Ratio Method

Extracted 50 μ g Cd⁺² (8.89×10^{-5} M) in (5ml) aqueous solutions at (pH_{ex}= 9) by (5ml) of ligand (BTABP) dissolved in chloroform at different concentrations (1×10^{-2} M – 1×10^{-6} M), after shaking the two phases for (10 minutes), separate aqueous phase from organic phase and determine absorbance of organic phase at ($\lambda_{max} = 520$ nm) which is the wave length of maximum absorbance for complex.

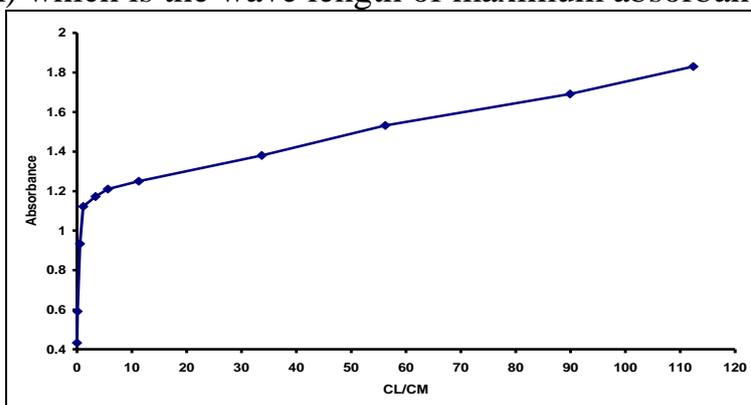


Figure (5): Mole ratio method for extraction Cd⁺² ions

This Figure shows the structure of ion pair complex extracted was (1:1) (ligand:metal) [Cd⁺²(BTABP)(Cl⁻)].

3.4.3. Continuous Variation Method

Prepared aqueous solutions for Cd⁺² ion in (1×10^{-4} M) and ligand solution dissolved in chloroform (1×10^{-4} M) also after that mixing different volume from these two solutions to maximum volume (5ml) at (pH_{ex}= 9) and shaking time (10 minutes), after complete shaking and separate two layers and determine absorbance to organic phase at $\lambda_{max} = 520$ nm for different mixing and plot Absorbance against V_m/V_T to get Figure (6), this Figure demonstrate the more probable structure of ion pair complex extracted was (1:1) ligand:metal [Cd⁺²(BTABP)(Cl⁻)].

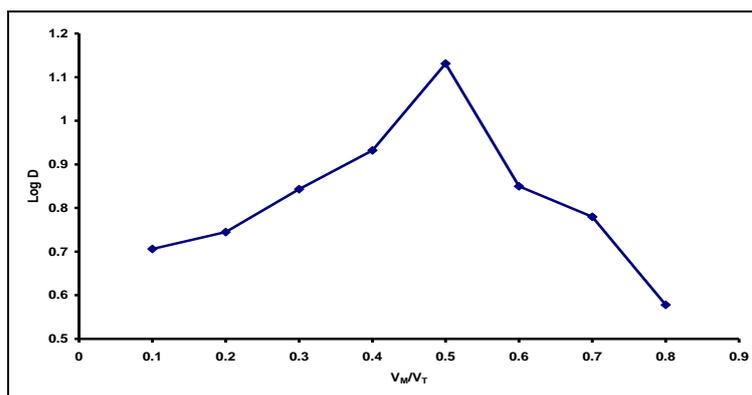


Figure (6): Continuous variation method for extraction Cd^{+2} ions

3.5. Organic Solvent Effect

Extracted ($50 \mu\text{g Cd}^{+2}$) ($8.89 \times 10^{-5} \text{ M}$) in (5ml) aqueous solutions at ($\text{pHex} = 9$) with (5 ml) of ($1 \times 10^{-4} \text{ M}$) ligand (BTABP) dissolved in different organic solvents differ in dielectric constant (ϵ), after shaking these two layers for (10 min.) and separate these two layers and calculate distribution ratio (D) get the result in Table (1) which shows that there is not any linear relation between distribution ratio values and dielectric constant (ϵ) for organic solvents, but there is an effect for organic solvent structure, and giving higher distribution ratio (D) with Toluene organic solvent, this result suggest participate organic solvent in structure of ion pair complex extracted.

Table (1): Organic solvent effect on extraction of Cd^{+2} ion

Organic solvent	(ϵ)	(D)
Dichloromethane	9.080	9.00
Chloroform	5.708	4.43
Bromobenzene	5.400	6.80
Benzene	2.804	11.50
Toluene	2.438	12.90
Carbon tetra chloride	2.380	10.90

3.6. Effect of Temperature on Extraction of Cd^{+2} Ions

Extracted ($50 \mu\text{g Cd}^{+2}$ ion) ($8.89 \times 10^{-5} \text{ M}$) in (5ml) aqueous phase at ($\text{pHex} = 9$) by (5ml) of ($1 \times 10^{-4} \text{ M}$) ligand (BTABP) dissolved in chloroform, after shaking these two layers at different temperature ($5^\circ\text{C} - 60^\circ\text{C}$) for (10 minutes), separate these two layers and calculate distribution ratio (D) at each temperature, afterward calculate extraction constant K_{ex} at each temperature with relation below:

$$K_{\text{ex}} = \frac{D}{[\text{Cd}^{2+}]_{\text{aq.}} [\text{BTABP}]_{\text{org.}}}$$

Plot $\log K_{\text{ex}}$ against $1/T$ °K get Figure (7) from the slope of straight line in Figure (7) calculate enthalpy of extraction ΔH_{ex} , for higher K_{ex} value calculate free energy of extraction ΔG_{ex} by relation below

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

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

As well as calculate ΔS_{ex} from relation

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

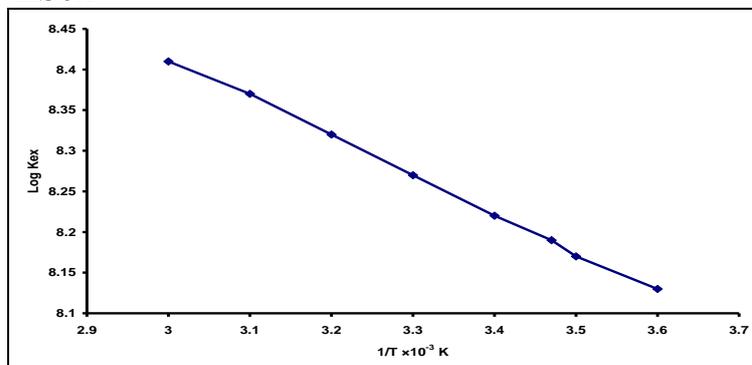


Figure (7): Relation between Log K_{ex} and 1/T °K

$$\Delta H_{\text{ex}} = 0.0087 \text{ KJ mole}^{-1}$$

$$\Delta G_{\text{ex}} = -52.4 \text{ KJ mole}^{-1}$$

$$\Delta S_{\text{ex}} = 157.4 \text{ JK}^{-1}\text{mole}^{-1}$$

The results shows the relation between ligand BTABP and Cd⁺² ions was endothermic reaction and low value of enthalpy emphasize the structure of ion pair association complex extracted was (1:1) as in stoichiometry [Cd⁺²(BTABP)(Cl)] and high value of entropy shows the reaction was entropic in region.

3.7. Synergism Effect

5 ml aqueous solutions contain 50µg Cd⁺² ions (8.89×10⁻⁵M) at (pH_{ex}= 9) extracted Cd⁺² ions by (5ml) of ligand dissolved in chloroform at (1×10⁻⁴M) and contain different concentration of Tributyl phosphate (TBP) dissolved in chloroform (1×10⁻⁶M – 1×10⁻²M), after shaking for (10 minutes) and separate organic phase from aqueous phase then calculate the distribution ratio in each concentration of TBP and plot log D values against log [TBP] to get Figure (8).

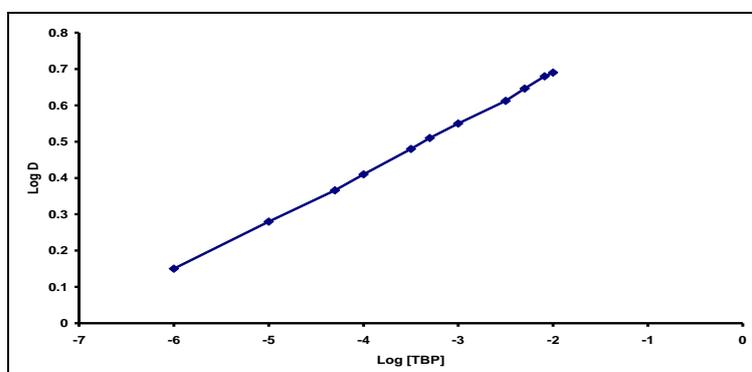


Figure (8): Effect of TBP concentration on distribution ratio

The results shows inhousement in distribution ratio (D) by addition (TBP) and distribution ratio increase with TBP concentration increase, from the slope of

straight line reflect there is one molecule of TBP participate in formation of one molecule of complex $[Cd^{+2}(BTABP)(Cl^{-})(TBP)]$.

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