Synthesis, Characterization and Structural Studies of Di benzyl dithiocarbamate and Use Them in CPE

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Abstract:
In this study the Cloud Point Extraction has been used as a separation technique that uses a surfactant instead of organic solvents for phase separation. CPE has also utilized as a pre-concentration strategy prior to the determination of trace levels of Copper and Nickel ions in water by flame atomic absorption spectrometry (FAAS). Di benzyl dithiocarbamate have been prepared from amines in the presence of sodium salts and carbon disulfide. The prepared compounds were characterized by means of Elemental Analysis, IR, ¹H NMR, Mass, and CHN spectroscopy. Application of the Cloud Point Extraction formation of the complexes dithiocarbamate with Copper and Nickel has been investigated, which was characterized by (UV-Vis), where it has been shown a stoichiometry of the complex. When Its ratio was 1:2, the results were identical to what is expected scientifically after studying the optimal experimental conditions. Then, the optimal conditions for the Cloud Point Extraction such as pH of the aqueous solution, concentration of the DDTC, amount of the surfactant, incubation temperature and time was covered. Under the optimal experimental conditions with a limit of detection, LOD at 0.012µg/ml, limit of quantization, LOQ, of 0.04µg/ml, and sensitivity of 5*10⁻³. The developed method was successfully applied for the determination of trace levels of lead ion in samples electrical power plant water.

Keywords: Cloud Point Extraction, Dithiocarbamate, Lead, Di benzyl dithiocarbamate

1. Introduction:

Dithiocarbamates: are of great agricultural, industrial, pharmaceutical importance due to their broad-spectrum antifungal activity, low acute toxicity, excellent metal chelating ability and low synthetic cost[1]. In this regard, the chronic dietary risk from DTCs residues was evidently underestimated[2]. Dithiocarbamate (R₂NCS₂⁻) ions strongly coordinate and stabilize metal ions in different oxidation states due to the high electron density on the sulphur atoms of the dithiocarbamato moieties[3]. Dithiocarbamate is an efficient metal-trapping agent because of its strong chelating ability, and it is therefore widely used in the treatment of metal contaminated wastewater. The chemical structure of dithiocarbamate is given in Fig. 1
Lanthanoid dithiocarbamate complexes have been studied sporadically since the 1960s. However, interest in these complexes has recently resurfaced for their practical application in catalysis, nanotechnology and microelectronics[5]. The dithiocarbamate ligands exhibit greater electron delocalization in their complexes around the MS2 bonds through CN and CS groups (Fig. 2).

Cloud point extraction: can constitutes an alternative to the conventional solvent extraction technique[7]. CPE technique exploits the heating operation of an aqueous solution of non-ionic surfactant, which becomes turbid at an appropriate temperature called the cloud point temperature (CPT), resulting in two aqueous phases[8]. A small volume of non-ionic surfactant-rich phase (coacervate phase) and an aqueous phase in which the non-ionic surfactant is at the concentration equal, or below to, its critical micelle concentration (CMC). Thus, the metal ions are extracted from the initial aqueous solution and it are concentrated into the coacervate phase by interaction with the micellar systems[9]. To improve and simplify traditional CPE, some improved CPE methods have been established, such as ultrasound–assisted CPE, mixed–surfactant CPE and ion–pair CPE[10]. Development of such a method is a challenging task because the molecular structures of dithiocarbamate only differ in the lengths of their alkyl chains, and most APs have alkyl-chain isomers. To date, two main analytical techniques, gas chromatography and high-performance liquid chromatography (HPLC) have been widely used for determination of trace DTCs[10].

Several non-ionic surfactants, such as Triton X-114, Triton X-100 or mixtures of both surfactants, PONPEs (polyoxyethylene-4-isononylphenoxyether) have been used for CPE procedures. Triton X-114 is the most common surfactant used for the separation of inorganic NPs by CPE[11]. CPE presents certain advantages compared to other conventional techniques (liquid-liquid extraction), such as lower cost, smaller volumes of solvents and the possibility of using less toxic reagents[12].

The following phenomenon explained the cloud point procedure (CPE) procedure (Figure 3): an aqueous solution with some surfactant becomes turbid and separates into two isotropic phases if some conditions such as temperature or pressure is changed or if an appropriate substance is added to the solution. The surfactant solution becomes turbid because it attains the cloud point. At this point, the original surfactant solution separates into a surfactant phase of small volume, which is rich in the surfactant and containing the analyte (parabens) trapped by micellar structures of the surfactant and a bulk diluted aqueous phase[13].
Fig 3: The steps of general procedure in CPE[14]

2. Material and methods:

2.1. Instrumentation:

The main instruments used in this research plan are as follows: FT-IR, UV-Vis, Mass, ¹H-NMR, FAAS, Molar Electrical Conductivity and Elemental Analysis.

2.2. Chemicals:

All chemicals used in this study were presented, used directly without any further purification (C₆H₅CH₂)₂NH, CuCl₂.6H₂O, Triton x-114, NiCl₂.6H₂O, Cadmium chloride hydrate, Lead Nitrate). All materials used are from well-known international companies and have a high purity of up to 99%.

2.3. Synthesis of reagent:

Sodium hydroxide (2 g, 0.05 mol) dissolved in a minimum amount of distilled water was allowed to achieve an ice temperature, cold carbon disulfide (3 mL, 0.05 mol) was added to the solution. This was then followed by the addition of di benzyl amine (10.6 mL, 0.05 mol). The mixture was stirred for (3-4 h) while keeping the temperature below 4 C0. A product was then filtered and washed with ether and dried in a desiccators. Fig. 4 shows the reaction. Yield=87%[15]
2.4. Primary testing of complex formation:

In a number of test tube added (1 ml) of metal solution (1x10^{-4}M) then added (1ml) of reagent solution (1x10^{-4} M) dropwise with mixing and the change of color is observed divided the solution in two halve add few drops of 0.05 M of NaOH for one halve and 0.05M of HCl

2.5. General Procedure of CPE:

A regular cloud point experiment needed the following steps: an aliquot of (10 ml) of a solution containing an of the metal ions solution in 1ml 5μg. 1.0 ml of (0.05 M HCl), (1.0 ml of 1×10^{-4}M) of reagent solution, 0.2% Triton X-114 was mixed. The mixture was moved for 1min and left to stand for 20 min regulated by the thermo-stated bath at 25°C until the production cloud point layer CPL. Separation of the two phases was completed immediately where the surfactant-rich phase displayed highly viscous and descended down at the bottom of the tube forming the aqueous phase that was simply discarded by decantation. After then, the surfactant rich phase in the tube was dissolved in 1ml of 1M HNO₃ in methanol and the absorbance of the resulting solution was estimated at by FAAS for extracted ion complex and with used calibration curve was measured the concentration of extracted metal ion amount, As the, determine the residual quantity of metal ion in aqueous solution after extraction by subtraction quantity of metal ion measured in the surfactant-rich phase from the initial quantity.

2.6. Optimization of the Parameters for CPE:

The effects of many experimental parameters that affect the CPE capability were given out by the classical optimization method. In as much as the extraction efficiency of the CPE depends on dual agents. Consequently, the effects of reagent concentration, HCl concentration, incubation time, equilibration temperature, Triton X-114 volume, and some other factors were selected in this study.

| No. | Modifying agent (0.1M) | Chemical formula |
|-----|------------------------|-----------------|
| 1   | Ammonium Nitrate       | NH₄NO₃         |
| 2   | Ammonium acetate       | C₂H₇NO₂        |
| 3   | lanthanum chloride     | LaCl₃          |
| 4   | Ammonium Sulfate       | (NH₄)₂SO₄      |

Table.2: Effect of Electrolytes Existence in Extraction Efficiency

| No. | Electrolyte(0.1M) | Chemical formula |
|-----|-------------------|-----------------|
| 1   | Potassium chloride| KCl             |
| 2   | Calcium chloride  | CaCl₂           |
| 3   | Magnesium chloride| MgCl₂          |
| 4   | Lithium chloride  | LiCl            |
| 5   | Sodium chloride   | NaCl            |

- Effect of reagent Concentration (1x10^{-4}, 5x10^{-4}, 1x10^{-3}, 5x10^{-3}, 1x10^{-2}, 5x10^{-2}M).
- Effect of HCl Concentration(2-10).
- Effect of the Incubation Time(10- 60 min).
- Effect of Equilibrium Temperature(20 – 80°C).
- Effect Triton X-114 Volume (0.5 – 3 ml).

Reagents and solutions:

1. Infrared spectra of the ligands and their suggested complexes

The daggers of the group C=N in the 3-chloro 4-methoxyphenyl dithiocarbamate appeared at (1631 cm\(^{-1}\)) respectively this is consistent with the literature. While group C-N daggers appear in the compound at (1511 cm\(^{-1}\)) respectively as well this is consistent with the literature. This is due to matrices of the C-N bond associated with sulfate in dithiocarbamate ligand, where the vibrations of this signal appear between the double finger C=N and the singles C-N in the complex prepared on the site (1635-1486 cm\(^{-1}\)), this is compatible with the literature.

![Fig 5: IR spectrum.](image)

2. \(^1\)H-NMR spectrum

The \(^1\)H-NMR spectrum appearance of di benzyl dithiocarbamate a signal at chemical shift (\(\delta\)) (5.3) ppm due to protons (CH\(_2\)-H), the appearance of a signal at (7.2 ppm) for the aromatic. The figure 6 shows that.

![Fig 6: \(^1\)H-NMR spectrum](image)

3. Mass spectra of reagent

Characterize mass spectra of the ligand appearance of molecular ion peak (M.\(^+\)) at 295 m/z and the spectrum show a series of peaks figure 7 at m/z = 273, 197, 121, 105, 91 and 77 corresponding to [C\(_{13}\)H\(_{22}\)N\(_2\)]\(^+\), [C\(_{13}\)H\(_{23}\)N\(_2\)]\(^+\), [C\(_8\)H\(_{11}\)N\(_2\)]\(^+\), [C\(_7\)H\(_9\)N\(_2\)]\(^+\), [C\(_7\)H\(_8\)]\(^+\) and [C\(_6\)H\(_6\)]\(^+\) respectively.
4. Elemental Analysis (CHNS)

The results of careful analysis of the elements there showed a kind match with the atomic weights that make up the compound, and the table(3), the results of the prepared compounds Di benzyl dithiocarbamate respectively.

| Elemental analysis (%) | Found | Cal. |
|------------------------|-------|------|
| Nitrogen               | 5.09  |      |
| Carbon                 | 37.40 |      |
| Hydrogen               | 2.79  |      |
| Sulphur                | 25.43 |      |

5. Ultra-Violate-Visible Spectra (determination of λ.max)

The aim of carrying out ultra-violet visible spectroscopic studies on sodium sulfadiazine was to confirm the presence of (S₂CN) moiety of di benzyl dithiocarbamate of π-π* and n-π* transitions. In the UV region, dithiocarbamates naturally show three bands. The intra-molecular intra ligand transitions matching to π = π* of the N-C=S system, π = π* of the S-C=S group and n = π* to be found on sulfur are assigned to these bands[16].
6. Stoichiometric Determination of complex (continuous variation method)

The continuous variation method was used for the determination of the stoichiometry of the complexes. A series of solutions were prepared, with constant molar concentration of metal and ligand. The absorbance recorded at $\lambda_{\text{max}}$. The results are showed that the M:L ratio for all complexes is 1:2, the results are tabulated in fig 9.

![Fig 9: Continuous variation method](image)

![Fig. 10: General structure of (C$_{30}$H$_{30}$N$_2$MS$_4$)](image)

Optimization of Cloud Point Extraction Procedure

The effects of several experimental parameters which impact the CPE efficiency were carried out by classical optimization (one-variable-at-a-time). In this approach, we observe the effect of one factor at a time on an experimental response. While only one factor is changed, others are kept at a constant level. Although, the optimization not ensure at all that the real optimum will be conformed, but it would be valid only if the variables to be optimized would be totally independent from each other (i.e. no interactive effects among the variables). Nevertheless, the classical optimization certainly leads at least to an improvement of the analytical method.

1. Effect of Electrolytes and Matrix Modifying Agent

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. An increase in the ionic strength in the CPE does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase
2. Study of Matrix Modifying Agent:

Volumes of 2ml with concentration 1% from different modifying agents as projected, modifying agent which give enhancement signal such as lanthanum chloride, Ammonium Nitrate and ammonium nitrate were used to overcome the interference. The modifying absorbance of 5 μg.ml$^{-1}$ of lead was studied in presence of modifying agent compare with the absorbance without using modifying agents. The result shows the enhancement of lead absorption signal by using Ammonium Nitrate as seen in fig 12.

3. Effect of reagent Concentration:

The effect of concentration of reagent on the analytical responses was consequently studied. Therefore, a set of similar experiments under the conditions of 1 μg.ml$^{-1}$Pb solution ion, 1%(v/v)Triton X-114, and varying concentration of (1×10$^{-4}$, 5×10$^{-4}$, 1×10$^{-3}$, 5×10$^{-3}$, 1×10$^{-2}$, 5×10$^{-2}$M) of reagent.
4. Effect of pH

The effects of pH of the watery plans on yield the extraction of Pb (II) as DDTC chelate was inquired about in pH run (2–10). The pH in 6 was chosen. The effect of pH on formation of Pb solution-reagent complex in Triton x -144 medium was determined by recording their absorbance signal in (pH 5).

5. Effect of equilibrium temperature:

The temperature was varied from 20 C° to 80 C° for 10. was observed due to very low number of micelles formed which cannot be able to encompass the ion-pair association complex at this temperature. But, at 60 C°. So, temperature of 25°C was chosen as optimum. as shown in Fig 2.
6. Thermodynamic Study

**Table 4: Variation of temperature for the extraction Pb**

| T / °C | T / °K | Absorbance | D       |
|-------|--------|------------|---------|
| 20    | 293    | 0.052      | 1.01    |
| 30    | 303    | 0.054      | 1.59    |
| 40    | 313    | 0.06       | 2.95    |
| 50    | 323    | 0.067      | 4.03    |
| 60    | 333    | 0.073      | 8.81    |
| 70    | 343    | 0.064      | 5.45    |
| 80    | 353    | 0.059      | 2.83    |

**Table 5: Variation of equilibrium constant with temperature during CPE.**

| T°C | 20 | 40 | 50 | 60 |
|-----|----|----|----|----|
| T°K | 293| 313| 323| 333|
| 1/T *10^-3 | 3.4 | 3.2 | 3.1 | 3 |
| D | 1.01 | 2.95 | 4.03 | 8.81 |
| KeX *10^7 | 0.164 | 1.292 | 1.421 | 5.312 |
| Log KeX*10^7 | 6.21 | 7.11 | 7.15 | 7.73 |

**Fig 2: Effect of equilibrium temperature.**

**Fig 3: Effect of the equilibrium extraction temperature on complex formation.**

\[
y = -3.5886x + 18.444 \\
R^2 = 0.9536
\]

\[
slope = \frac{-\Delta H_{ex}}{2.303 R}
\]
Table 6: Thermodynamic parameters.

| T K  | ΔH<sub>ex</sub> (KJ mol<sup>-1</sup>) | ΔG<sub>ex</sub> (KJ mol<sup>-1</sup>) | ΔS<sub>ex</sub> (Jmol<sup>-1</sup>) |
|------|-----------------------------------|-----------------------------------|-----------------------------------|
| 293  | 0.0677                            | -34.4                             | 117.6451                          |
| 313  |                                   | -37.37                            | 127.7474                          |
| 323  |                                   | -43.6                             | 149.0102                          |
| 333  |                                   | -48.55                            | 165.9386                          |

The value of enthalpy change (ΔH<sub>ex</sub>) was obtained from the plot of log K<sub>ex</sub> versus 1/T (Fig 3) and found to be 0.0677 kJ mol<sup>-1</sup> while the values of Gibbs free energy (ΔG<sub>ex</sub>) were obtained at different temperatures. Once these two parameters are obtained, the values of entropy change (ΔS<sub>ex</sub>) were also calculated and all the data are shown in Table.

The results revealed that the extraction of ion-pair complex is easy and thermodynamically favorable and resulting in increasing the phasevolume ratio thus extraction efficiency. The extraction process is endothermic in nature. It was also noted from (Table ) that the values of ΔG<sub>ex</sub> approximately increased with temperature. The negative values of ΔG<sub>ex</sub> indicate that the ion-pair complex solubilization process is also spontaneous and thermodynamically favorable. The reaction of extraction by CPE is endothermic reaction and positive value of ΔS<sub>ex</sub> means the reaction is entropic in region.

7. Effect of Incubation Time:

The effect of time on the extraction in the range of (10 - 50) min was investigated by taking 10ml aqueous solution and followed CPE procedure.

![Fig 4: Effect of Incubation Time.](image)

8. Effect of Triton X-114 Volume:

The used in CPE to form the surfactant-rich phase the effect of Triton X - 114 concentration was investigated between (0.2-3.5) ml of triton X-114 (1% v/v) in 10ml aqueous solution containing 1.5 µgml<sup>-1</sup> Pb<sup>2+</sup>, and subjected to general CPE procedure.
9. Calibration curve of determination Lead (II) ion:

The results were shown in Fig 6. Very good linearity was obtained in the concentration range of (0.05 -1) µg/ml for Pb with coefficient of determination (R²) of 0.988 and the limit of detection (LoD = 0.012µg/ml) and limit of quantitation (LoQ = 0.04µg/ml) achieved from Pb solution with DDTC reagent by developing CPE- AAS and the analytical are summarized in (Table ). Some characteristics of Cloud point extraction include that it is: inexpensive, simple, sensitive and rapid system in pre concentration and separation of trace metal. Furthermore, for pre-concentration of 10 ml of the working standard solutions based on the slope ratio of calibration curves with and without pre-concentration and was obtained for Pb solution Fig 6.

To test the reproducibility of the proposed extraction method, the suggested procedure was repeated eight times under optimum conditions. The relative standard deviation (R.S.D.) was measured for 0.9 ng.ml⁻¹ to be 1.01 %.

| No. | Parameters                             | Value      |
|-----|----------------------------------------|------------|
| 1   | Pb hallow cathode lamp element (nm)    | 283.1      |
| 2   | Sample volume (ml)                     | 10ml       |
| 3   | Chelating agent 5*10⁻³M                | 1ml        |
| 4   | PH                                     | 5          |
| 5   | Incubation time (min)                  | 15min      |
| 6   | Water bath heating temperature(°C)     | 60°C       |
| 7   | Triton X-100 (2%)                      | 1.5ml      |

Table 7: Optimum conditions
|     |                                             |     |
|-----|---------------------------------------------|-----|
| 8   | Slope with pre-concentration                 | 0.745 |
| 9   | Slope without pre-concentration              | 0.044 |
| 10  | Enrichment factor (Slope of CPE/Slope of Normal) | 16.9 |
| 11  | Correlation coefficient ($R^2$)               | 0.991 |
| 12  | Sensitivity ($4 \times 10^{-3}$)              | $5 \times 10^{-3}$ |
| 13  | Concentration range $\mu g \cdot ml^{-1}$    | ($0.05 - 1$) $\mu g/ml$ |
| 14  | Limit of detection ($3\sigma$/slope) $\mu g \cdot ml^{-1}$ | 0.012μg/ml |
| 15  | Limit of quantitation ($10\delta$/slope)$\mu g \cdot ml^{-1}$ | 0.04μg/ml |
| 16  | RSD% ($n=8$) at 0.05μg.ml$^{-1}$              | 1.03 |

### Application of real samples

The near electrical power plant pollution of river water was estimated and samples were taken from different sites, the first It's about 1 km south of Al-Nasiriya city before electrical power plant. the second It is discharge hot water to the river, the third It lies about 3 km after electrical power plant.

**Table 8: Recovery percentage of the Lead ion real samples.**

| Sample            | type | Cd Add | Cd Found | % Recovery | % Error |
|-------------------|------|--------|----------|------------|---------|
| The first station | soil | 0      | 0.44     | -          | -       |
|                   |      | 0.5    | 0.94     | 100.78     | 0.78    |
|                   | water| 0      | 0.23     | -          | -       |
|                   |      | 0.5    | 0.73     | 101.48     | 1.48    |
| The second station| soil | 0      | 0.52     | -          | -       |
|                   |      | 0.5    | 1.02     | 102.01     | 2.01    |
|                   | water| 0      | 0.51     | -          | -       |
|                   |      | 0.5    | 1.01     | 100.38     | 0.38    |
| The third station | soil | 0      | 0.87     | -          | -       |
|                   |      | 0.5    | 1.37     | 101.18     | 1.18    |
|                   | water| 0      | 0.64     | -          | -       |
|                   |      | 0.5    | 1.14     | 101.48     | 1.48    |
| The fourth station| soil | 0      | 0.7      | -          | -       |
|                   |      | 0.5    | 1.2      | 101.83     | 1.83    |
|                   | water| 0      | 0.56     | -          | -       |
|                  |      |        | 1.06     | 103.1      | 3.1     |

### 3. Conclusion:

The combined advantages of the cloud point methodology (easy, safe, rapid and inexpensive) and the use of dithiocarbamate as a reagent (selectivity and sensitivity) for Pb$^{2+}$ were and soil utilized for their determination in water samples. The main advantage of the method is simultaneous determination of traces of lead without the need for any chemometric method. The method gives a very low limit of detection and good R.S.D. values. The results of this study clearly show the potential and versatility of this method, which could be applied to monitoring lead spectrophotometrically in various water samples.
4. Acknowledgements:

The authors gratefully acknowledge the support of this work by Basra University Research Council.

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