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Extractive desulfurization of model diesel oil by using novel indolium based ionic liquids

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ABSTRACT

A new type of organic salt of indolium and its complex salts have been recently the subject of intensive research or the extractive desulfurization of model oil (Dibenzothiophene DBT), due to the limitation of hydrodesulfurization process for removing sulfur compounds catalytically. The ionic salt of the type $[L]_2[MCl_2I_2]$ (where L = cations of N-methyl indolium $[MHIn]^+$, M = Mn(II), Co(II), Ni(II), and Cu(II)) were obtained using (2:1) molar ratio. The prepared organic salt and its complex salts were characterized by elemental analysis, IR, conductivity measurement, electronic spectra, metal content analysis and magnetic measurements. The conductance data indicate that the organic salts are (1:1) electrolyte whereas the complex salt s are (2:1) electrolyte and (1:1) for iron complex. The electronic spectra and magnetic measurements indicate that the anion of the type $[MCl_2I_2]^{-2}$ and $[FeCl_3I]^-$ have a tetrahedral environment around the metal ions.

Keywords: desulfurization, ionic liquids.

INTRODUCTION

Ionic liquids are mixtures of salts with low melting points. Because of their salt-like characteristics, they are nonvolatile and nonflammable and exhibit a high ionic conductivity. The liquid phase is found over a wide temperature range up to 300 °C. IL's are generally highly solvating and non-coordinating (1–3) . Both the cations and anions of the salt determine the physical properties (e.g., melting point, viscosity, density, solubility, etc.). For cations organic salt-forming compounds (e.g., pyridine, imidazole, etc.) are often chosen. The anion moiety often consists of inorganic anion-forming components (AlCl3, BF3, AgBF4, etc.). Depending on the ratio of cation/anion the IL can be Lewis-acidic, neutral, or Lewis-basic (4). Recently, ionic liquids were found to be effective in the desulfurization of model diesel fuels (dibenzothiophene (DBT)/*n*-dodecane) under mild conditions(5-11). Other studies tested IL's on real gasoline and/or diesel samples and various IL's. Because of new and stringent regulations, desulfurizing of fuels has become increasingly important to the petroleum industry. In refineries, hydrotreating is a commonly used method to reduce sulfur in fuels. Unfortunately, the associated costs (e.g., equipment and hydrogen) are high. Newly developed methods can also achieve deep desulfurization of gasoline but are less effective for diesel fuels (12-16). Certain sulfur compounds in diesel are less prone to react and remain in the fuel. An associated problem is the cross-contamination of fuels during pipeline transportation. Low sulfur fuels that exit a pipeline at terminals may contain unacceptable high sulfur levels. Thus, an effective and easily applicable method needs to be found that can lower or remove sulfur-containing compounds while not affecting the fuel properties themselves. Extracting these sulfur compounds from true fuels with IL's could offer such a solution (17). In this paper, we use a kind of quaternary ammonium coordinated IL [MHIn]I and its transition metals complex salts as the catalyst for the desulfurization of model diesel oil, which have been prepared by using (dibenzothiophene (DBT)/*n*-hexane) .

EXPERIMENTAL PART

Preparations of the Compounds

The compounds were prepared according to literature procedures (18-20).

Preparation of Indole Salts:

1-Methyl indolium iodide salt [MHIn]I **(L)**: This salt was prepared by adding (0.01 mol, 1.17 g) of indole dissolving in (10 ml) of ethanol to (0.02 mol, 2.84 g) of methyl iodide in a (50 ml) round bottom flask. The mixture was refluxed for (2 hours), then it was extracted with equal volume of normal hexane (3-5) times in order to remove the excess amount of methyl iodide. The solution volume was concentrated to half and left for one day. Light brown powder was obtained, filtered and washed several times by diethylether.

Preparation of Complex Salts

Preparation of $[MHIn]_2\,[MnCl_2I_2]$ **(1)**: (0.005 mol, 0.99 g) of $MnCl_2.4H_2O$ was dissolved in (10 ml) of water then added to (0.01 mol, 2.59 g) of compound **(1)** dissolved in (20 ml) of ethanol. The mixture refluxed for (2 hours). The product solution concentrated to half volume and left for one day for standing. Dark brown powder was obtained; it was filtered and washed several times by diethylether.
Following the same procedure **(2, 3, 4)** complex salts were prepared, when the equivalence of transition metal ion is two times the molar ratio of transition metal chloride to organic salt 1:2 in case of M(II), and when the equivalence of transition metal ion is three times the molar ratio of metal chloride to organic salt 1:1 in case of Fe(III). The micro elemental analysis shows that the compounds have good matching with the suggested structure. The physical properties and the yields, chemical formula, conductivity, magnetic properties and the elemental analysis are shown in Table (1).

Desulfurization of Fuel

The desulfurization of fuel include the extractive of organic salts and complex salts with model fuel in order to optimize the best compounds for testing on real diesel oil (21-26).
The model diesel oil contained (3000 ppm) of (DBT) and it was prepared by dissolving dibenzothiophene (DBT) in n-hexane by weights. All the prepared compounds were tested for extractive desulfurization by using model fuel with the same concentration and the same time (10 g of model fuel, with 0.05 g of compound was dissolved in 5 ml of DMSO , 30 min of extraction), in order to optimize the best compound and make another testing with a different concentration and a different time and make another test of different concentration.

Physical Measurements

Elemental analysis of the organic salt and its isolated complexes were accomplished by using (Flash EA 1112 Series, Thermo electron corporation). Metal content estimation were done by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on (SPECTRO CIROS CCD). The infrared spectra for ligand and complexes were recorded on a JASCO Canvas FT/IR 4200 at the range (200-4000 cm^{-1}) without using KBr or CsI . GC-Mass Spectrometer done by using (Trio- 1000 Mass spectrometer. Proton Nuclear Magnetic Resonance (^{1}H-NMR) by using DMSO-d6 as solvent at (20 ^{o}C) on (BRUKER AVANCE DPX 400 MHz). Gas Chromatography – Flame Ionization Detector (GC- FID) The Gas Chromatography was carried out by using (CARLO ERBA STRUMENTAZIONE 4200). This measurements were carried out in Liverpool university, department of chemistry.

The programs temperature are :

Injector temperature : 295 ^{o}C ,Detector temperature : 273 ^{o}C

Oven temperature : 130 ^{o}C for 2 min then ramping till 175 for 10 min.
Gases flow rate details :

Hydrogen : 1 kg / cm^2, Make up (air) : 1 kg / cm^2 , Air : 1.5 kg / cm^2

Helium : 2 kg / cm^2

Column properties :

Name: SE-30, Length : 30M, diameter: 0.53 mm, Film thickness : 1.2 µm All these measurements were carried out at Department of Chemistry, university of Liverpool.

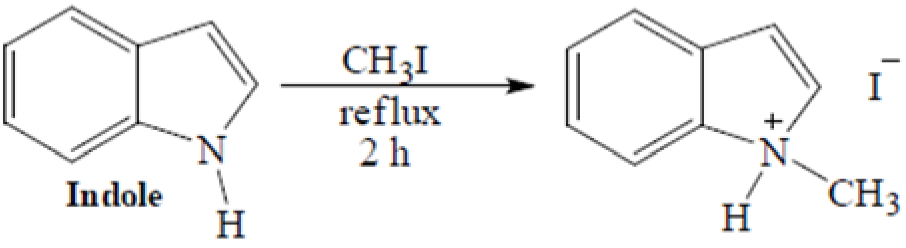
Conductivity measurements for 10^{-3} M solution of the complexes in (DMF) were carried out on Jenway 4510 conductivity meter. The UV/Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10^{-3} M solution of the complexes in DMF using 1 cm quartz cell . Magnetic susceptibililties values were corrected for diamagnetic contribution using Pascal's constants and measured at 25□ C on the solid state using Bruker B.M.6 instruments .

Table 1: Analytical data and physical properties of the prepared compounds

No.	Chemical formula	M. P. °C	Color	Yield	Elemental analysis (found) / calculated				µ eff (B.M)	Λ (10^{-3}M) $Ohm^{-1}.mol^{-1}.cm^{2}$
					C%	H%	N%	M%		
L	[MHIn]I $C_9H_{10}NI$	79-85	Brown	85	42.88 (46.85)	4.17 (4.74)	5.26 (5.23)	---	---	67
1	$[MHIn]_2[MnCl_2I_2]$ $C_{18}H_{20}N_2MnCl_2I_2$	153-155	Dark brown	55	33.57 (33.85)	3.60 (3.52)	4.17 (4.16)	8.17 (8.27)	6.10	157
2	$[MHIn][FeCl_3I]$ $C_9H_{10}NFeCl_3I$	300 <	Dark brown	75	25.66 (25.70)	2.39 (2.54)	3.32 (3.24)	13.26 (12.87)	5.51	75
3	$[MHIn]_2[CoCl_2I_2]$ $C_{18}H_{20}N_2CoCl_2I_2$	147-150	Black	55	33.36 (33.67)	3.58 (3.31)	4.14 (4.13)	9.09 (9.50)	4.30	168
4	$[MHIn]_2[CuCl_2I_2]$ $C_{18}H_{20}N_2CuCl_2I_2$	169-172	Light brown	85	33.13 (33.93)	3.09 (3.03)	4.29 (4.01)	9.34 (9.43)	2.10	92

RESULTS AND DISCUSSIONS

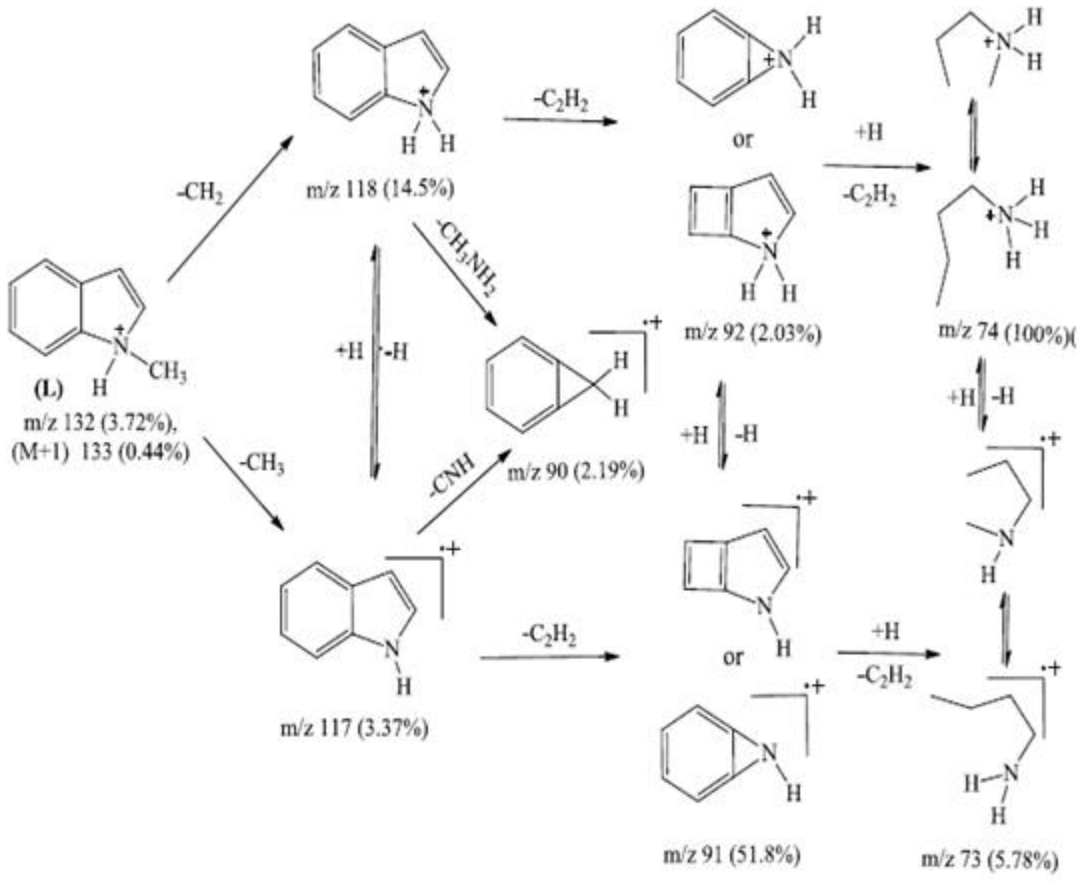
The prepared organic salt and complex salts were characterized by using various physical and spectroscopic methods, the elemental analysis has a good matching with the suggested ratio (1:1) of cations species in this organic salt. The result depends on reaction pathway, which is going through addition reaction of methyl group on nitrogen in indole as shown
in Scheme (1) :



(1)

Scheme 1: Synthesis path for the preparation of organic salt (L)

Scheme (2) show the suggested fragments of organic salt (L) , according to the reference (27). Fig (1) show the fragmentation diagrams of organic salt (L). The proton nuclear magnetic resonance spectra (^{1}H- NMR) of organic salt (L) by using DMSO-d_6 as solvent, the two single bands in (2.73 ppm) and (2.89 ppm) with integrations of (2.94) and (3.18) respectively. From this chemical shift and integration, these bands belong to two methyl groups protons on nitrogen atom. From the chemical shift and integration of two multiple bands in (6.89-7.10 ppm) with integrations (0.968) and (1.05), these bands belong to two protons of (CH) groups in heterocyclic ring of Indole. The multiple bands in (7.26 -7.56 ppm) with integrations of (4.11) belong to the four protons of benzene aromatic ring in indole. The final band in (7.96 ppm) with integration of (1.16) belongs to proton of (NH) group (19,20,28). The singlet band in (2.51 ppm) belongs to d_6-DMSO and the broad band in (3.53 ppm) belongs to water. Fig (2) shows (^{1}H-NMR) spectra of organic salt (L).



Scheme 2: The suggested cation GC-Mass fragmentation mechanism diagram of [MHIn]I (L)

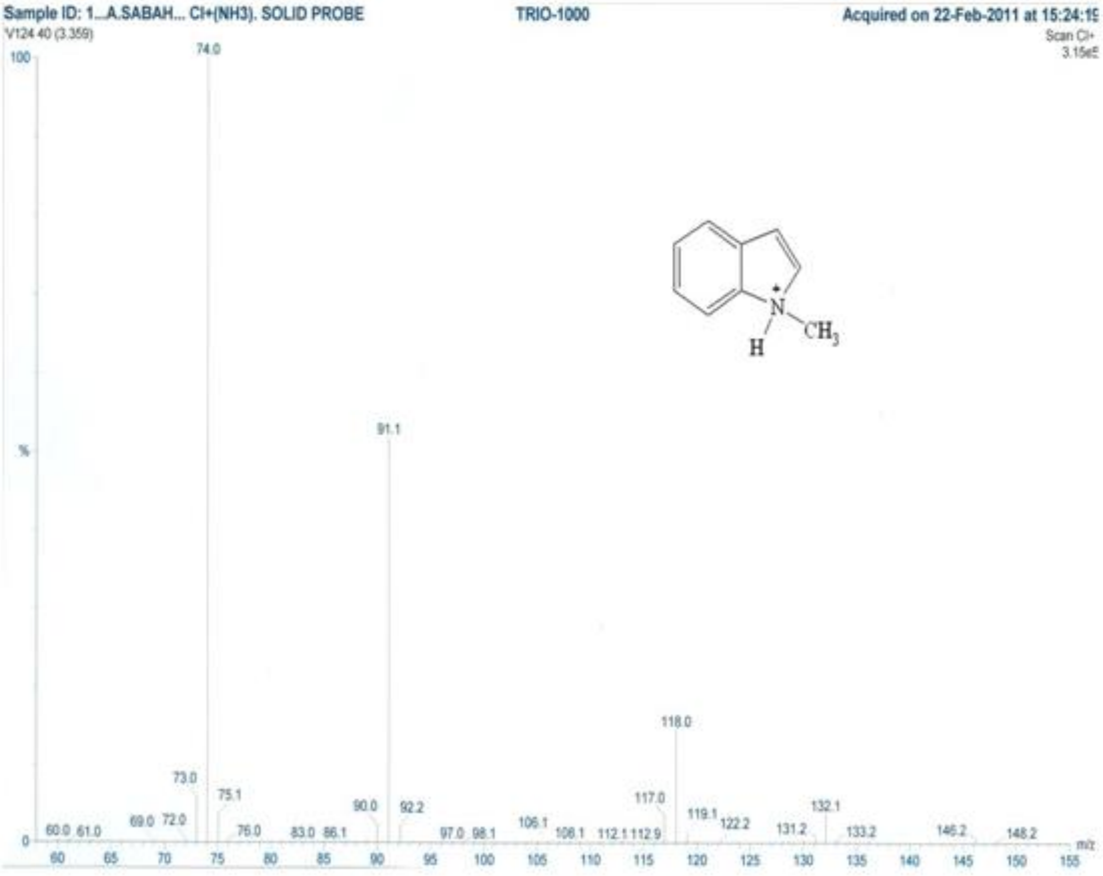


Fig 1: GC-Mass spectra diagram of [MHIn]I (L)

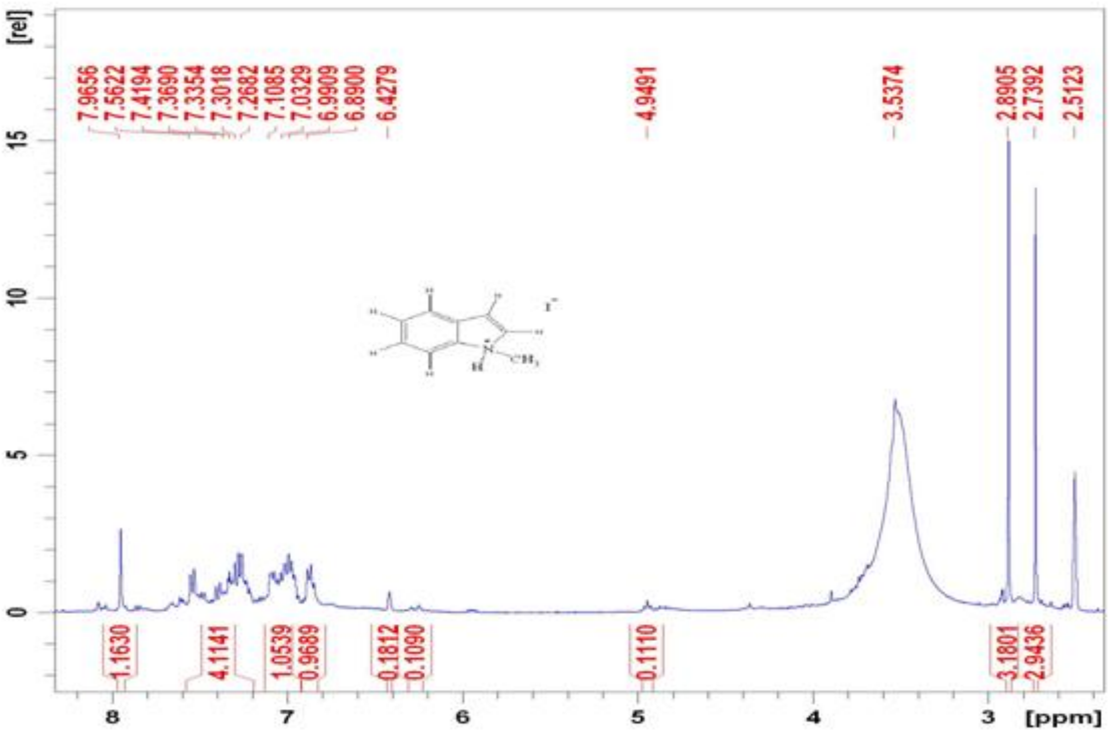


Fig. 2: (^{1}H-NMR) spectra of [MHIn]I (L)

The electronic spectra organic and ionic salt $^{(29)}$ are listed in Table (2). The organic salts showed a band at (36101 cm^{-1}) assigned to π-π* or n-π*.

Infrared spectrum has been recorded in the range (200-4000 cm^{-1}) of the IR spectrophotometer and has been used in order to identify the prepared organic salts and complex salts$^{(30)}$. The values and positions of the spectra bands are tabulated in Table (3).

Table 2: Electronic spectra (cm^{-1}) of manganese (II) complexes

Compound No.	bands	
L	---	36101
1	24200	28248
2	20576	29411
3	15243	---
4	14782	30864

Table 3: Groups stretching frequencies value for the prepared compounds cm^{-1}

No.	υ(N$^+$-H)	υ(N$^+$- CH$_3$)	υ(C=C)	υ(C-H)	υ(M-X)
L	2560 s	2361vw	1624 s	3004 w	---
1	2555 m	2360 w	1637 m	3020 s	220m, 300m
2	2490 w	2390 m	1640 w	2977 s	210 m, 290 s
3	2409 w	2359 m	1622 m	2977 s	220m, 305s
4	2530 s	2485 m	1635 s	3010 s	222m, 290s

vw = very weak, w=weak, m= medium, s= strong

UNEXPECTED RESULTS

The recrystallizations of complex salt number (5) resulted in unexpected green-yellow crystal containing only from the nickel (II) chloride salt with two molecules of water and two of solvent molecules (DMF) as shown in Fig (3). The organic salt used in the preparation may be removed by the solvent of recrystallizations as shown in result of single crystal x-ray diffraction:

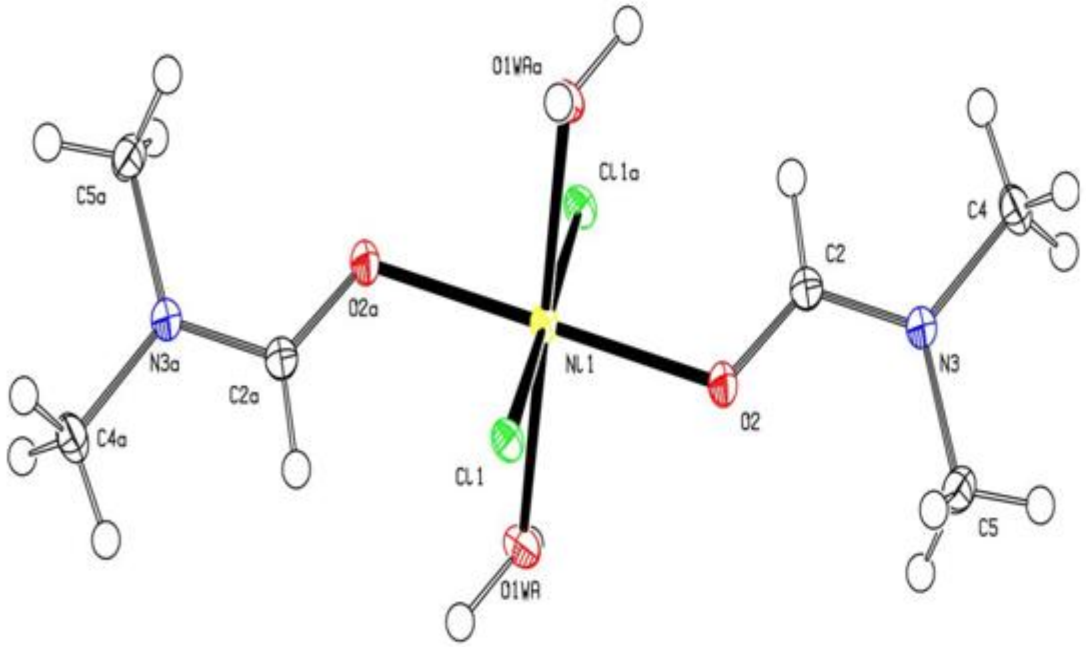


Fig. 3: The crystal structure of compound (5) $[NiCl_2.(H_2O)_2.(DMF)_2]$

The Desulfurization of Model Diesel Oil

For model diesel oil, the treatment has been carried out for several concentrations and several time after making calibration curve using gas chromatograph technique (31-35).

The calibration curve diagram was made from the relation between the ratio of area of the standard Dibenzothiphene (DBT) peak over area of the celebrants Hexadecane (C16) peak (Fig 4) and the concentration of the stander solution as shown in Table (4) and Diagram (1).

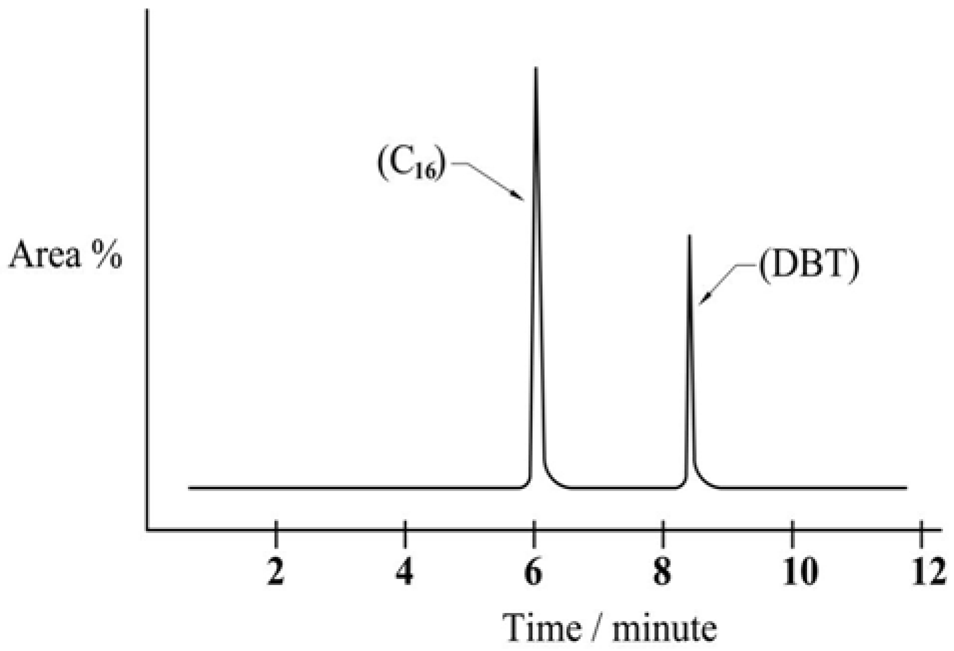


Fig 4: Retention time and relative area under the peak of (DBT) and (C16).

Table 4: The relative area of (DBT) over (C16) and the concentration of stander solution

Conc. (ppm)	DBT / C16	C16 %	DBT %
4000	1.8568	207314	384958
3000	1.3963	226161	315797
2000	1.0131	141492	143349
1000	0.5847	135207	79067
500	0.2294	133305	30586

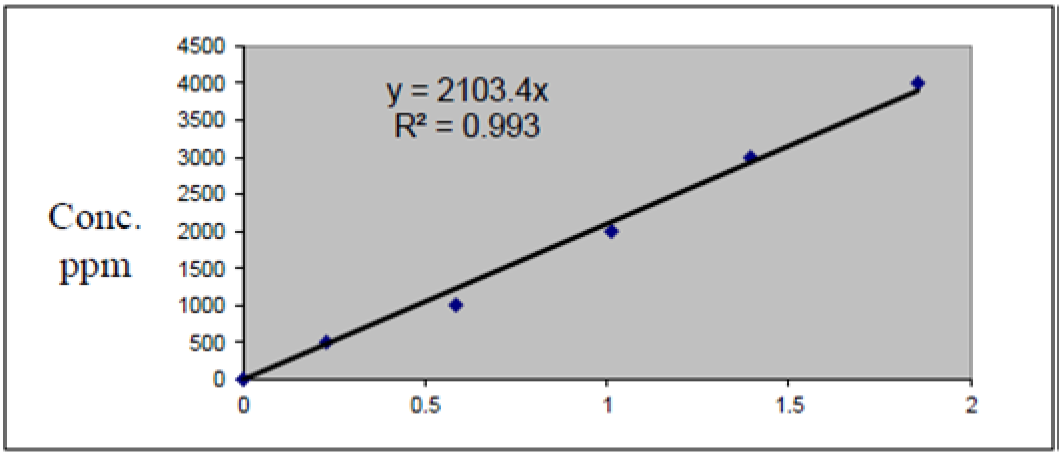


Diagram 1: Calibration curve of stander solution

All the prepared compounds were tested in the extraction process for 30 min with the same concentration of the prepared compounds (0.05g) in order to optimize the best compound for the next treatment, Table (5).

Table 5: The removal sulfur % for 30 min and (0.05g) extractive treatment

No.	DBT %	C16 %	DBT/C16	DBT conc.	S removal %
1	106412	218212	0.4877	1025.7319	34.0111
2	91375	156628	0.5834	1227.0997	21.0564
3	113599	153475	0.7402	1556.8929	0.0000
4	86962	163628	0.5315	1117.8763	28.0831
5	91530	165345	0.5536	1164.3787	25.0914

CONCLUSION

All the results of the complex salts confirm the tetrahedral geometry around the metal center . The prepared compounds have different efficiency for desulfurization because the different anion or cation causes different interaction with organ sulfur compounds in diesel oil. In the desulfurization of model diesel oil, we obtained higher percentage of removal sulfur rather than the real diesel oil. That may because of the variety of the compounds in the real diesel oil, but in the model, there is one compound containing the sulfur (DBT) which represents all organ sulfur compounds in the model.

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