



Preparation of Some Mercurated Dowex Resins and Study of Their Industrial Applications For Desulfurization

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ABSTRACT

During this research some chemical modifications especially (mercuration) have been done on Dowex resin.

It is known that the sulfur dioxide gases are the main source of acid rain and air pollution, result from the conversion of fuels containing sulfur compounds in combustion engines. As a result of environmental impact, strict requirements on low sulfur content in fuels are becoming prominent throughout the world.

This study was carried out to remove dibenzothiophene from model light oil (benzene containing DBT, 3080 ppm. sulfur content) by using the mercurated Dowex. The analysis of the resulting treated DBT solution to know the sulfur concentration was obtained by using atomic absorption

The mercurated polymers were identified spectroscopically using infrared spectroscopy.

Keywords: Dowex, desulfurization, mercurated polymers.

تحضير بعض راتنجات الدوكس الحاوية على الزئبق و دراسة تطبيقاتها الصناعية في إزالة مركبات الكبريت

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الملخص

خلال هذا البحث تم إجراء بعض التحويرات الكيميائية خاصة (تفاعل الزئبق) على راتنج الدوكس. أجريت هذه الدراسة لإزالة dibenzothiophene من نموذج محضر للنفط الخفيف (البنزين المحتوي على DBT، 3080 جزء في المليون كبريت) باستخدام راتنج الدوكس الحاوي على الزئبق. تم استخدام جهاز الامتصاص الذري لمعرفة تركيز الكبريت في محاليل ثنائي بنزوثايوفين بعد المعاملة مع البوليمرات الحاوية على الزئبق. كما تم تشخيص البوليمرات المحضرة باستخدام طيف الاشعة تحت الحمراء. الكلمات الدالة: راتنجات الدوكس ، إزالة مركبات الكبريت ، البوليمرات الحاوية على الزئبق .

1. Introduction

Crude oil is the largest and most widely used as source of energy in the world. However, such crudes contain sulfur, typically in the form of organic sulfur compounds. The sulfur content and the API gravity are two properties which have a great influence on the value of the crude oil. The sulfur content has been determine as a percentage of sulfur by weight and varies from less than 0.1% to more than 5% depending on the type and source of crude oils [1].

The most abundant heterocyclic sulphur compounds identified in petroleum includes sulfides, thiophenes, benzothiophenes and naphthobenzothiophenes.

During the partial or complete combustion of a sulfur-containing residual oil, the sulfur gets converted to SO₂ and SO₃ (typically referred to as SO_x). During the combustion or pyrolysis process, the sulfur emissions from a typical high sulfur residual oil can be extremely high; additional processes such as flue gas desulfurization are needed to clean up these emissions and bring the SO_x content of effluent gases to acceptable levels. This requires an additional investment of capital, as well as additional operating expense, to continue operating industrial units that use the sulfur-containing residual oil [2]. One of the easily and fast method to remove sulfur from diesel oil is the adsorption desulfurization process[3].It is one of the methods which can be used to achieve ultra-low sulfur content in diesel fuel. It is considered the most effective method for the removal of the trace amounts of residual sulfur in fuels after hydro desulfurization treatment [4]. Chemical modification of polymers is one of the methods used to synthesize new polymeric compounds. It is the most active fields of research in polymer sciences for the past 30 years and enables us to introduce functional or reactive groups into polymers, to alter polymer surfaces, to provide side chain substituents. Important products of polymer modification include polymeric reagents, functionalised resins, catalyst and media for trapping reaction intermediates organometallic polymers acid carrier for active molecules [5]. The mercuration of polymers is a suitable method for the preparation of selective adsorbents [6].More particularly, the invention relates to a new class of homo and copolymers which contain mercuric ions aromatically bound therein. The products produced in accordance with this invention find utility as carries in biopolymer applications, i.e. as carrier gels for removing sulfur-containing groups from mixtures, in tracing studies, as carrier for biologically active substances and the like [V].

2. Experimental Part

2.1. Materials and instruments

All the chemicals used have been supplied by Fluka and Aldrich.

Infrared spectra have been recorded by shemadzue FT-IR-8400 s Fourier transform Infrared spectrophotometer in the range between (4000-250 cm^{-1}).

Varian-AA-240FS Fast Sequential Atomic Absorption Spectroscopy, Australian, used for measuring the concentration of mercury and sulfur ions in solutions in N.G.C / Kirkuk-Iraq.

All the samples have been dried under reduced pressure at 50-65 C° .

2.2. Mercuration of Dowex(-SO₃Na) Using Mercury acetate in Dioxan (C-1)

(2.0620 g) of Dowex (-SO₃Na) were added to (10 ml) of Dioxan in a (250 ml) flask with stirring for (30 min) at room temperature, then (3.1868 g) of mercury acetate and (2 ml) acetic acid were added to the reaction mixture. The content was refluxed for (24 hrs) and the resulting mixture poured into a (200 ml) of water. The polymer were collected and washed with excess of water until the removal of unreacted mercury and then with methanol. The weight of product after drying was (2.4076 g).

2.3. Acidification of Dowex(-SO₃Na) (C-2)

(10 ml) of (18%) HCl was added to (10 g.) of Dowex (-SO₃Na) in round bottomed flask. The reaction mixture was refluxed in a water bath at (50 C°) with constant stirring for (2 hrs). The resultant mixture was filtered and washed well with distilled water several times until the removal of acidity. The weight of product after drying was (8.4925 g).

2.4. Mercuration of Dowex(-SO₃H) Using Mercury Oxide in THF (C-3)

(1.8421 g) of Dowex (-SO₃H) were added to (10 ml) of THF in a (250 ml) flask with stirring for (30 min.) at room temperature. Then, (2.1659 g.) of mercury oxide and (8 ml) acetic acid were added to the reaction mixture. The content was refluxed for (24 hrs) and the resulting mixture poured into a (200 ml.) of water. The polymer was collected and washed with excess of water until the removal of unreacted mercury and then with methanol. The weight of product after drying was (3.1291 g).

2.5. Nitration of Dowex (C-4)

(13.9 ml) of concentrated nitric acid was mixed with (15.2 ml) of concentrated sulphuric acid in round bottomed flask in ice bath, then (6 g.) of Dowex was added. The reaction mixture was refluxed in a water bath at (70 C^o) with constant stirring for (7 hrs) and the resulting mixture poured into a (75 ml) of water. The polymer was collected and washed with excess of water several times until the removal of acidity and washed with methanol. The weight of product after drying was (5.2842 g).

2.6. Mercuration of Nitrated Dowex Using Mercury Oxide in Dioxan (C-5)

(.2921 g) of nitrated Dowex (-SO₃H) were added to (10 ml) of Dioxan in a (250 ml) flask with stirring for (30 min.) at room temperature. Then, (2.1659 g) of mercury oxide and (8 ml) acetic acid were added to the reaction mixture. The content was refluxed for (24 hrs) and the resulting mixture poured into a (200 ml) of water. The polymer was collected and washed with excess of water until the removal of unreacted mercury and then with methanol. The weight of product after drying was (3.3470 g).

2.7. Desulfurization (Using Different Conditions)

Time:- (10 ml) Solution of (Dibenzothiophene in Benzene) (3083 ppm sulfur) was mixed with (0.1 g) of polymer (all mercurated Dowex resins) in a round bottomed flask with stirring for (4,8,12,16,20,24 hrs) at room temperature. The resulting solution was filtered to separate the polymer from the filtrate. The filtrate was analyzed for sulfur content.

This step is to choose the proper contact time that gives highest sulfur removal.

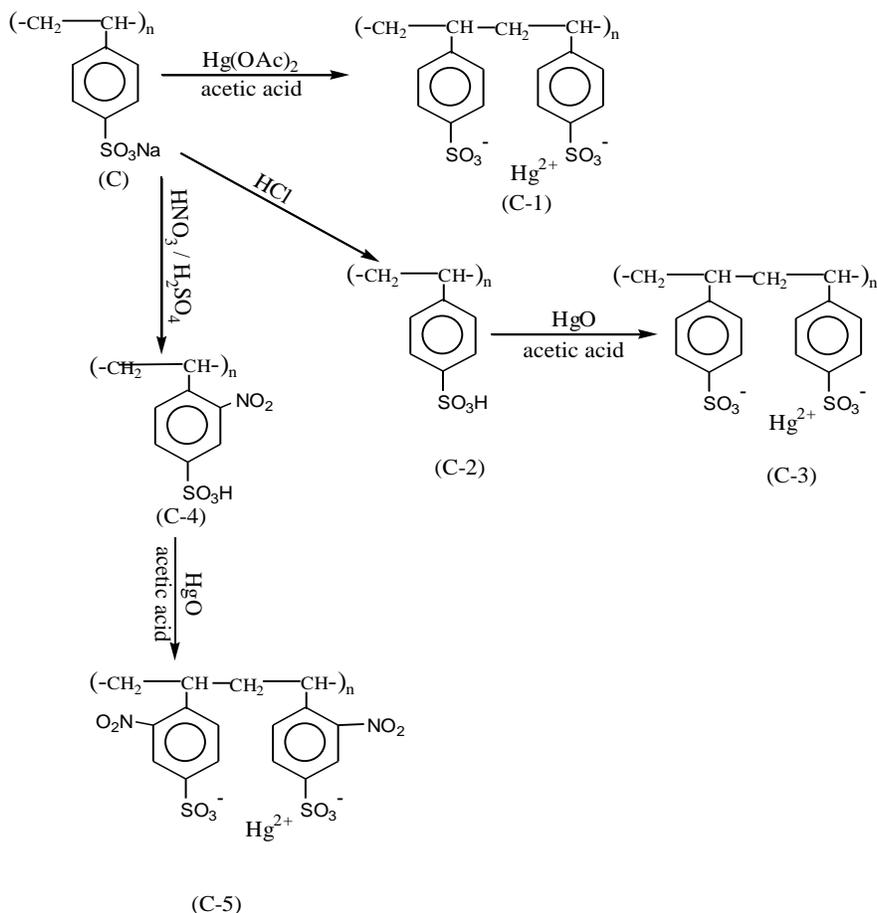
Temperature:- (10 ml) Solution of (Dibenzothiophene in Benzene) was mixed with (0.1 g) of polymer (all mercurated Dowex resins) in a round bottomed flask with stirring for (24 hrs) with raise the temperature to (35 C^o) and (50 C^o). The resulting solution was filtered to separate the polymer from filtrate. The filtrate was analyzed for sulfur content.

This step is to choose the proper temperature that gives highest sulfur removal.

The Amount Of Absorbent:- (10 ml.) solution of (Dibenzothiophene in Benzene) was mixed with (0.1,0.3,0.5 g) of polymer (all mercurated Dowex resins) in a round bottomed flask with stirring for (24 hrs.) at (50 C^o). The resulting solution was filtered to separate the polymer from filtrate. The filtrate was analyzed for sulfur content.

This step is to choose the proper amount of absorbent that gives highest sulfur removal.

3 .Results and Discussion



Scheme (1): Expected chemical structure of modified polymers prepared from Dowex.

3.1. Mercuration of Dowex(-SO₃Na) Using Mercuric acetate (C-1)

Mercuration of Dowex(-SO₃Na) by using mercuric acetate was achieved when Dowex was mixed with dioxane and added to mercuric acetate with reflux for (24 hrs.), as shown in **scheme (1)** .

The IR spectrum of free Dowex (-SO₃Na) (sodium-poly-p-vinylbenzylsulfonate) and mercurated Dowex can be compared with each other to check spectral changes.

An important spectral change observed between the spectrum of free Dowex and the mercurated Dowex investigated here is the shifting of a splitting band observed at $1687\text{-}1645\text{ cm}^{-1}$ in free Dowex to lower wave number band at 1627 cm^{-1} .

It was observed an increase in the weight of product, which indicates the entry of mercury in the copolymer structure. Percent mercury was equal to (12.66%), as it shown in [Table \(3-1\)](#).

3.2. Acidification of Dowex(-SO₃Na) (C-2)

Dowex which is an ion-exchange resin has many applications in the medical and industrial field, so it is used the study.

The cationic Dowex that have sulfonic acid groups (-SO₃H), instead of sodium sulfonate (-SO₃Na) is prepared by the reaction of Dowex (-SO₃Na) with hydrochloric acid (18%).

The IR spectrum of the acidified Dowex is showed (S=O) asymmetric stretching vibration at 1215 cm^{-1} and (S=O) symmetric stretching vibration at 1029 cm^{-1} .

3.3. Mercuration of Dowex(-SO₃H) Using Mercury oxide (C-3)

This reaction is obtained by treated Dowex, a sulfonated polystyrene resin, with mercuric ions to produce a mercurated resin, as shown in [scheme \(1\)](#).

The IR spectrum of free Dowex (-SO₃H) and mercurated Dowex (-SO₃H) can be compared with each other to check spectral change.

An important spectral change observed between the spectra of free Dowex (-SO₃H) and the mercurated Dowex (-SO₃H) investigated here is the shifting of a band observed at 1631 cm^{-1} in free Dowex (-SO₃H) to higher wave numbers and its splitting in to bands at 1652 cm^{-1} and at 1560 cm^{-1} .

Also it was observed an increase in the weight of product, which indicates the entry of mercury in the copolymer structure. Percent mercury was equal to (20.26%), as it shown in [Table \(3-1\)](#).

3.4. Nitration of Dowex(-SO₃Na (C-4))

The nitration has been carried out using a mixture of concentrated sulfuric acid and concentrated nitric acids, as shown in [scheme \(1\)](#).

The product was analyzed for nitrogen which was (6.52%).

The IR-spectrum of nitrated Dowex showed the characteristic absorption bands of nitro groups at 1531 cm^{-1} for (N=O) asymmetric stretching vibration and at 1361 cm^{-1} for (N=O) symmetric stretching vibration in addition to the (-SO₃H) bands.

3.5. Mercuration of Nitrated Dowex Using Mercury oxide (C-5)

Nitrated Dowex is also mercured by treating the nitrated Dowex with mercuric ions to produce a mercured resin, as shown in [scheme \(1\)](#) .

The IR spectrum of nitrated Dowex and mercured resin can be compared with each other to check spectral change. An important spectral change observed in the spectra of nitrated Dowex (-SO₃H) and the mercured resin investigated here is the shifting of a band observed at 1531 cm^{-1} in nitrated Dowex to higher wave number at 1537 cm^{-1} . Also it was observed an increase in the weight of product, which indicates the entry of mercury in the copolymer structure. Percent mercury was equal to (5.33%), as it shown in [Table \(3-1\)](#).

3.6. Desulfurization

All mercured Dowex resins were used to desulfurize the solution of (dibenzothiophene in benzene 3083 ppm sulfur).

Time:- The desulfurization time was (4,8,12,16,20,24 hrs),almost all polymers which were used for desulfurization gave the proper contact time that gives highest sulfur removal at room temperature was (24 hrs), as shown in [Table \(3-2\)](#), so the best time that uses for desulfurization was (24 hrs). It was found that the stirring for (24 hrs) is enough to get reasonable sulfur removal.

Temperature:- By raising the temperature of desulfurization from room temperature to (35 C°) and (50 C°). It was observed a better desulfurization, as shown in [Table \(3-3\)](#).

The amount of absorbent:- (0.1,0.3 and 0.5g) of polymers were mixed with solution of (dibenzothiophene in benzene), for (24 hrs), at (50 C°) with continuous stirring and then filtration process have been done. The filtrate was analyzed for sulfur content and the results are shown in [Table \(3-4\)](#).

Table (3-1): Hg% in mercurated polymers and degree of substitution

<i>Polymers</i>	<i>Hg %</i>	<i>Ds %</i>
C-1	12.66	13.09
C-3	20.26	23.21
C-5	5.33	6.44

Table (3-2): Sulfur concentration in (dibenzothiophene solution) after treatment with mercurated polymers at different Time

Polymer	Time (hr.)	Sulfur (ppm)
C-1	4	3013.01
	8	2821.25
	12	2699.78
	16	2564.46
	20	2492.21
	24	2487.06
C-3	4	2994.17
	8	2701.22
	12	2425.49
	16	2161.31
	20	1992.92
	24	1988.04
C-5	4	3076.12
	8	2956.28
	12	2901.33
	16	2843.45
	20	2766.54
	24	2764.77

Table (3-3): Sulfur concentration in (dibenzothiophene solution) after treatment with mercurated polymers at different Temperatures

Polymer	Temperature (C ^o)	Sulfur (ppm)
C-1	25 (room temp.)	2487.06
	35	2322.07
	50	2301.39
C-3	25 (room temp.)	1988.04
	35	1643.99
	50	1571.21
C-5	25 (room temp.)	2764.77
	35	2664.44
	50	2661.63

Table (3-4): Sulfur concentration in (dibenzothiophene solution) after treatment with mercurated polymers by using different amount of mercurated polymers

Polymer	Absorbent (g)	Sulfur (ppm)
C-1	0.1	2301.39
	0.3	2234.06
	0.5	2201.11
C-3	0.1	1571.21
	0.3	1303.34
	0.5	1006.87
C-5	0.1	2661.63
	0.3	2643.31
	0.5	2601.65

References

- [1] A. Al-Malki, M. Sc. Thesis, “*Desulfurization of Gasoline and Diesel Fuels, Using Non-Hydrogen Consuming Techniques*”, King Fahad University of Petroleum and Minerals, (2004).
- [2] S. Chavan, H. Kini and R. Ghosal, “*Process for Sulfur Reduction from High Viscosity Petroleum Oils*”, International Journal of Environmental Science and Dvelopment, 3, 3, (2012).
- [3] I. A. H. Al Zubaidy, F. B. Tarsh, N. N. Darwish, B. S. S. Abdul Majeed, A. AlSharafi and L. Abu Chacra, “*Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials*”, Journal of Clean Energy Technologies 1, 1, (2013).
- [4] M. Xue, R. Chitrakar, K. Sakane, T. Hirotsu, K. Ooi, Y. Yoshimura, M. Toba and Q. Feng, J. Colloid Interface Sci., 298, 535, (2006).
- [5] W. M. Wanyunus, Chemical Modification of Polymers: *Current and Future Routes for Synthesizing New Polymeric Compounds*, (2002).
- [6] J. Baldrian, H. P. Gregor and J. Stamberg, Collect. Czech. Chem. Commun., 36, 4054-4056, (1971).
- [7] T. G. Traylor, *Mercuration of Aromatic Polymers*, Journal of Polymer Science, 37, 132, (1959).

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