

The synthesis of an ester based on maleic anhydride. Application to lead extraction

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Abstract— The industrial wastes of heavy metals constitute a major problem for the environment which is in particular dependent, with the toxicity of certain chemical elements. So the selective elimination of the water-soluble metal cations represents an important issue. In a concept of “depollution”, an original approach utilizes the possibility of complexing metals. This work deals with the field of the macromolecular chemistry, which provides many examples of complexes, by synthesizing one of the derivatives of alkenylmaleic anhydride; and belongs to the family of esters capable to chelate of the lead's cations ; and the rate of extraction has been approximately 85%.

Index Terms— Alkenylation, depollution, ion exchange, extraction, heavy metals.

1 INTRODUCTION

The problem of environmental pollution is still relevant because many industrial activities continue to generate various pollutants consisting in particular, of heavy metals whose may create significant nuisance [1, 2]. Faced with the more restrictive regulations, manufacturers must necessarily treat their effluents before reintroducing them into nature. For this, various techniques of purification are used [3, 4, 5, 6]. The toxicity of heavy metals [7, 8] has led governments to regulate emissions by setting maximum limits. A decree of February 2nd, 1998, related to the installations which are classified for environmental protection, and fixe any kind of emissions must respect the comply of these facilities. The order does not define heavy metals but selects a number of areas with environmental restrictions of metals. One example is the pollutants emission in water limits: Twelve metals are concerned: Aluminum, Arsenic, Cadmium, Chromium, Nickel, Copper, Tin, Iron, Manganese, Mercury, Lead and Zinc. They have toxic effects even the state of traces, [9], however, at present, the development of clean technologies is increasingly desired to preserve the environment. It is in this context that our petrochemical synthesis Laboratory, has set an objective to develop a remediation technique by simple extraction, efficient and environmentally friendly with an anionic surfactant body which is an ester based on maleic anhydride. This work focuses on the thermodynamic and physicochemical properties of anionic body, especially the clearance of contaminated solutions by metal pollutants.

And this paper deals with the synthesis of the acid salt of bi-ethyl decanilmaleiate part family of anionic body: type carboxylates.

The synthesis of this ester involves the following steps:

- (i) alkenylation Reaction from maleic anhydride, and decene for obtaining decanilmaleic anhydride,
- (ii) esterification reaction of the anhydride dècanilmaléique and ethylèneglycol to obtain bidecanilmaleiate ethyl acid and
- (iii) neutralization reaction of the acid functions of the bi-dècanilmalèiate ethyl acid, by caustic soda, to obtain the acid salt bi-dècanilmalèiat ethyl which is soluble in water.

1. Materiel and methods :

1.1. Synthesis of an ester based on maleic anhydride:

The ester based on maleic anhydride which belongs to the family of anionic surfactant, carboxylate-type (succinates or succinimides) and finds many practical applications, and can be obtained in three steps: [10,11]

- (i) The first step is a reaction of Alkenylation between maleic anhydride and a mono or poly-olefin in order to obtain the alkenyl maleic anhydride.
- (ii) The second step is a reaction of esterification of alkenyl maleic anhydride with fatty alcohol, or a poly alcohol to obtain a mono or polyesters.
- (iii) The third step is a reaction of neutralization of poly or mono es-

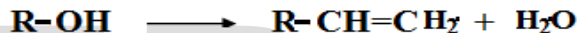
ters obtained in second step with caustic soda.

2. 1.1. Synthesis of anhydride decanilmaleic:

The alkenylation reaction is just condensation of maleic anhydride and decene-1, resulting from the dehydration of decanol-1.

A. The raw material preparation:

The dehydration of decanol -1 occurs according to the following general reaction:



With: Decanol-1 à 99, 99% of purity; Catalyst (granulated alumina).

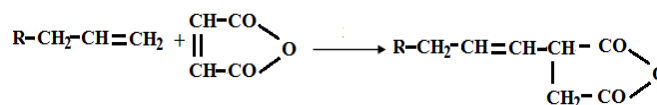
The product obtained was identified by iodine value analysis (table1).

Table 1: Decene-1 yield [%]

Sample	Molecular Mass	Index of saponification	Active matter yield [%]
I	238	275.37	58
II	238	278.70	58.7
III	238	276.-80	58.3

B. Alkenylation of maleic anhydride by decene-1:

The alkenylation reaction can be written as follows:



Reagents used: maléique Anydrid and decene-1 in order to obtain decanilmaléique anhydride

The characteristics of the decanilmaléique anhydride product by this reaction are shown in Table2.

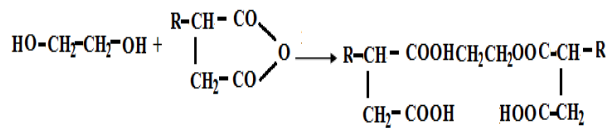
Table -2 : Decanilmaleic anhydrid. Characteristics.

sample	molecular Mass	Index of saponification	active matter yield [%]
I	238	275,37	58
II	238	278,70	58,7
III	238	276.-80	58,3

2.1.2. Esterification of the decanilmaléique anhydrid and ethylèneglycol:

A. Synthesis of ethyl bi-dècanilmalèiate acid:

The samples obtained are in turn used in the synthesis of the anhydride decanilmaléique derivatives such as esters.



(i) Conducting the experiment:

2 moles of anhydride and decanilmaléique, 1 mole éthylène glycol are introduced into the reactor containing the solvent; then they are heated to the temperature of the esterification reaction (140 to 120 °C) for 6 hours.

(ii) Purification of the esterification product :

After the esterification, the reaction mass subjected to a vacuum of 2mmHg at 96 °C, for one hour to remove the ethylene glycol does not react, with the solvent, then the mixture is cooled in an inert medium.

The material balance of the esterification reaction is as follows: **table 3**

Table 3: Total area of the esterification reaction

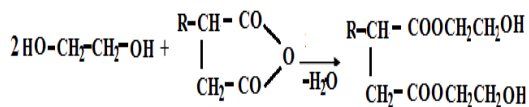
(Reagents + products) esterification	Initial quantities	Final quantities [g]	Product yield [%]
bi-decanilmaléique anhydrid at. 58%	96,55	20,27	79
Ethylène glycol	7,52	1,58	
ethyl bi-decanilmaléiate acide at	0,00	114,04	

Also we can represent the bi-decanilmaléiate ethyl acid characteristics in **table 4**;

Table 4: Characteristics of the bi-decanilmaléiate ethyl acid

esterification product	Performance of active ingredient in%	Acid index		Index of saponification	
		theoretical	Pratice	Théorique	Pratique
ethyl bi-decanilmaléiate acide	44,82	92,08	91,98	161,57	160,05

The Synthesis of di-ethyl decanilmaléiate is performed according to this reaction:



3.1.3. Neutralization of the bi-decanilmaléiate ethyl acid by soda:

The neutralization reaction is carried out in the presence of sodium hydroxide, potassium hydroxide, etc.. For reasons of solubility of this product in water, it is preferred to use sodium hydroxide. The neutralization reaction is as follows:

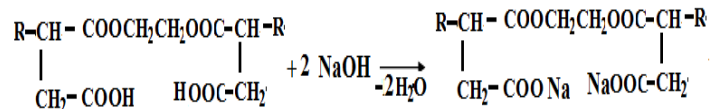


Table 5: Total field of the neutralization reaction

ethyl bi-decanilmaléiate [g]	theoretical soda Quantity [g]	Amount of added soda (practice) [g]
30	4,25	4,68

2.2. Determination of the critical micelle concentration (CMC) of ethyl bi-decanilmaléiate acid salt:

The measurement principle is to balance using electromagnetic balance, and the surface tension forces. The apparatus used is a tensiometer LAUDA TD1, based on the Wilhelmy method; it is added by a very thin blade plate, and specially etched perfectly wettable. The blade is drawn violently in contact with the surface of the solution, the equilibrium is re-established by applying a force equal to the product of the force "F" (in dynes) which attracts the blade length "L" (cm) and negligible thickness 'e': $\gamma = F / 2(L+e) \sim F / 2L$.

We prepare For each surfactant a series of aqueous solutions from a stock solution. The concentrations ranging from 10⁻⁷ to 10⁻² mol / l were performed on each bottle as a sample 0.1 ° C. is introduced into a vessel thermostated at ± 0,1 °C.

We proceed by measuring the surface tension using the method described above. Its value is calculated by the formula. We repeat the process for each solution. The set of values of the surface tensions obtained allowed us to trace the isothermal curves which are the logarithm of each compound concentrations. The breakpoint of the curve shows the value of the critical micelle concentration (CMC) of the test substance. **Fig 1**

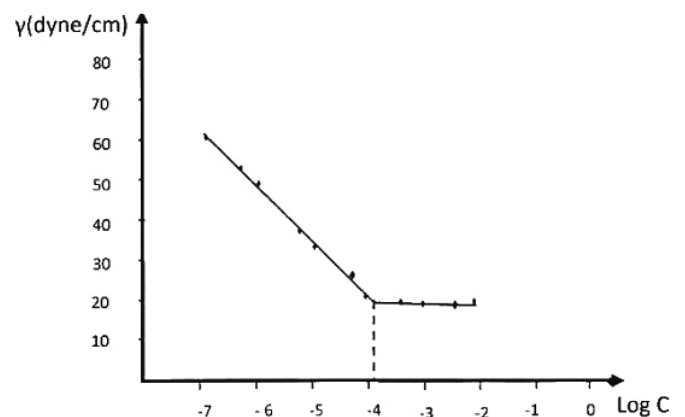


Figure 1 : Changes in surface tension of bi-ethyl decanilmaléiate vs. Log of C at 20 °C.

The value of the CMC salt obtained was $1.25 \cdot 10^{-4}$ mol / l. This value is approximately 100 times lower than that of conventional ionic compounds. This is due to the very nature of hydrophobic compound (presence of two long hydrocarbon chains). This result leads to the formation of large aggregates that could attach large amounts of metal ions to form insoluble complexes and very stable in water. The high value of the slope of the curve reflects the high surface activity.

2.3. Operating tests synthesized product as an extractant of heavy metals

2.3.1. Preparation of solutions.

Determination of Ca^{2+} and Mg^{2+} ions in distilled water:

By means of a pipette of 100 ml, for distilled water in three conical flasks. It was added to each flask, 5 ml of ammonia buffer solution (pH = 9.3) and a black color pinch for staining. Titrate the solutions obtained by the solution of complexone III (EDTA) at 0, 1 N to turn the color from pink to blue.

2.3.2. The lead (II) dosage by spectrophotometry:

A. Spectrophotometry:

The spectrophotometer used is PU.8600 type UV / VIS. The law of Beer Lambert establishes a relationship between the optical density (absorbance) of a solution and its concentration. It is defined by the following formula:

$$A = \epsilon \cdot L \cdot c$$

Where, A is the absorbance of the solution, L is the length of the optical path, C is the concentration of solution and ϵ is the molar extinction coefficient.

The lead (Pb^{2+}) can be measured spectrophotometrically [13], because it reacts quickly and completely with dithizone (HDz) to form a colored complex extractable $PbDz_2$, by carbon tetrachloride. The reaction of complex formation is represented by the balanced equation:



B. Spectrophotometer calibration:

(i) Reagents used are dithizone solution in a 10^{-2} CCl_4 , ammonia buffer to 20% and solution lead to dose

(ii) Blank test to perform the test blank, the device was calibrated with a free solution of lead which is a white test (5 ml solution to 10^{-2} mol / l of dithizone in CCl_4 + 5 ml of ammonia buffer at 20% + 5ml distilled water)

(iii) The sketch of reference Graph: In a separating funnel, 5 ml are collected aqueous solution containing the ions Pb^{2+} assay. We add 5 ml of ammonia buffer (pH = 9.3) and then 5 ml of dithizone solution in carbon tetrachloride. It was stirred and then the two phases are separated and measured at 520 nm absorbance. Only the colored complex $Pb(DZ)_2$ absorb at this wave length.

The procedure for the determination of the complex solution obtained from the prepared one after the other solutions (from the lower concen-

tration ($5 \cdot 10^{-7}$ mol / l) to the most concentration (10^{-3} mol / l) by UV-Vis. The results obtained are shown in the following table: 6

Table 6 ; Absorbance of the solutions of different Pb^{2+}

$[Pb^{2+}]$ ion/g/l	$5 \cdot 10^{-7}$	10^{-6}	$5 \cdot 10^{-6}$	10^{-5}	$5 \cdot 10^{-5}$	10^{-4}	$5 \cdot 10^{-4}$
Absorbance	0,070	0,130	0,200	0,260	0,320	0,390	0,525

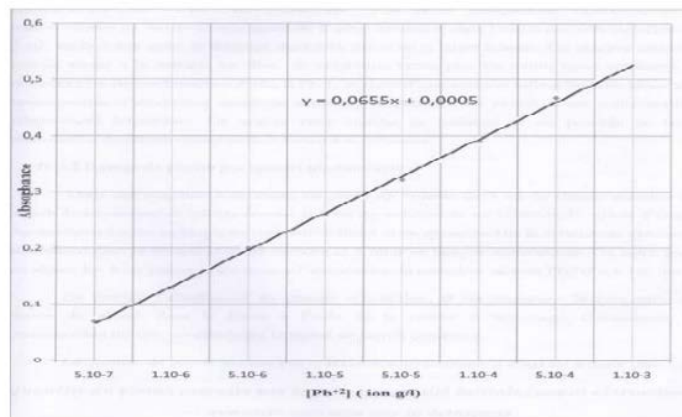


Figure 2: Absorbance of(dithizone-lead) complex in function of concentration of lead

It is noted that the absorbance varies linearly with the solutions concentration of lead. So we can deduce the lead concentration for each solution if we know its absorbance (in the same conditions).

2.3.3. Test extraction of lead by ethyl bi-décanylmaléiate acid salt:

A. Preparation of samples ethyl bi-décanylmaléiate acid salt:

We have considered a determined volume of each lead solution of a known concentration ($5 \cdot 10^{-4}$, 10^{-4} , $5 \cdot 10^{-5}$, 10^{-5} , $5 \cdot 10^{-6}$, 10^{-6} , $5 \cdot 10^{-7}$ and 10^{-7} ion g / l .) and we have added the same volume of ethyl bi- décanylmaléiate acid salt solubilized in water at a concentration of $5 \cdot 10^{-3}$ mole /l. The mixture was stirred for 10 min and allowed to stand. Atomic absorption is observed after a certain time at the surface, a film of brown color is more or less thick containing the complex [(bi-décanylmaléiate ethyl) Pb] analysis of a small amount of this phase spectroscopy showed the presence of lead to a relatively large concentration. This mixture layer was separated and extraction tests proceeded to lead the remaining solution with dithizone

B. The lead dosage by spectrophotometry:

In a separatory funnel, it takes a volume of 5 ml of each solution of known initial lead concentration and 5 ml of ethyl bi- décanylmaléiate acid salt. After separation, the mixture is collected and the filtrate is added 5 ml to the solubilized solution of dithizone in carbon tetrachloride and 5 ml of ammonia buffer. It was stirred and then the two phases were separated and the absorbance of the complex obtained $Pb(DZ)_2$ is measured at 520 nm.

The absorbance of each sample was measured, and the exact concentration of lead in the filtrate was determined using the calibration curve. Knowing that the initial concentration, determine the mass of lead com-

The amount of the extracted lead by the bi-ethyl decanilmaleiate salt is given by:

$$\text{Amount of lead extracted by salt} = \frac{\text{initial amount (before extraction)} - \text{Quantity extracted by dithizone}}{\text{Quantity extracted by dithizone}}$$

The calculation of the rate of extraction is given by the following formula:

$$\text{extraction rate} = \frac{\text{amount of Pb}^{2+} \text{ extracted by salt}}{\text{initial amount}}$$

The results of calculation are given in **Table7**

Table 7 : Influence of lead concentration on the extraction rate for a concentration of ethyl bi-décanylmaléiate acid salt equal to 5.10⁻³ mol/l.

[Pb ²⁺]mol/l	2,5.10 ⁻⁷	5.10 ⁻⁷	2,5.10 ⁻⁶	5.10 ⁻⁶	2,5.10 ⁻⁵	5.10 ⁻⁵	2,5.10 ⁻⁴	5.10 ⁻⁴
Quantity of Pb ²⁺ with g in 5ml.	2,6.10 ⁻⁷	5,2.10 ⁻⁷	2,6.10 ⁻⁶	5,2.10 ⁻⁶	2,5.10 ⁻⁵	5,2.10 ⁻⁵	2,6.10 ⁻⁴	5,2.10 ⁻⁴
Absorbance	0,050	0,070	0,170	0,175	0,225	0,229	0,375	0,410
Quantity of Pb ²⁺ extracted with dithizone	2,6.10 ⁻⁷	5,2.10 ⁻⁷	2,04.10 ⁻⁶	2,2.10 ⁻⁶	0,45.10 ⁻⁵	0,8.10 ⁻⁵	0,44.10 ⁻⁴	1,7.10 ⁻⁴
Quantity of Pb ²⁺ extracted with ethyl bi-décanylmaléiate acid salt	00,00	00,00	0,56.10 ⁻⁶	3,00.10 ⁻⁶	2,00.10 ⁻⁵	4,40.10 ⁻⁵	2,16.10 ⁻⁴	3,50.10 ⁻⁴
Extraction rate	00%	00%	21%	58%	82%	85%	83%	67%

We noticed that the extractions of Pb²⁺ begin at values between 2.6. 10⁻⁶ and 5, 2.10⁻⁷ g. These relatively small amounts show that the complex formed has a priori, a low stability constant even if the ring closure upon complexation is advantageous from energy point of view. The highest rate is obtained for a lead quantity of 5, 2. 10⁻⁵ g although the amount of salt is very important. It is therefore interesting to optimize the amount of salt for quantitative extraction.

2.3.4. Influence of the concentration of bi-décanylmaléiate ethyl acid salt on the extraction of lead:

The minimum amount of the complex agent that can extract a maximum amount of lead is an important factor in our work. For this, we varied the bi-décanylmaléiate ethyl acid salt concentration of: 10⁻²; 5.10⁻³; 10⁻³; 5.10⁻⁴; 10⁻⁴ and 5.10⁻⁵ mol / l, so to obtain salt in the minimum quantity of bi-décanylmaléiate ethyl acid salt at which maximum extraction. the results of extraction are given in the following **table 8**.

Table 8: Influence of the concentration of bi-ethyl decanilmaleiate acid salt ,the extraction rate of lead:

m [bi-ethyl decanilmaleiate acid salt] mol/l	5.10 ⁻³	2,510 ⁻³	5. 10 ⁻⁴	2,5. 10 ⁻⁴	5. 10 ⁻⁵	2,5. 10 ⁻⁵
m [bi-ethyl decanilmaleiate acid salt]in 5ml of solution	1,46.10 ⁻²	7,32.10 ⁻³	1,46.10 ⁻³	7,32.10 ⁻⁴	1,46.10 ⁻⁴	7,32.10 ⁻⁵
mPb ²⁺ (g) before extraction in5ml of solution	5,2.10 ⁻⁵	5,2.10 ⁻⁵	5,2.10 ⁻⁵	5,2.10 ⁻⁵	5,2.10 ⁻⁵	5,2.10 ⁻⁵
absorbance	0,229	0,230	0,231	0,297	0,311	0,320
mPb ²⁺ (g) extracted with dithizone	0,8. 10 ⁻⁵	0,8. 10 ⁻⁵	0,85. 10 ⁻⁵	3. 10 ⁻⁵	5,05. 10 ⁻⁵	5,2. 10 ⁻⁵
mPb ²⁺ (g) extracted with our salt	4,4. 10 ⁻⁵	4,4. 10 ⁻⁵	4,35. 10 ⁻⁵	2,2. 10 ⁻⁵	0,15. 10 ⁻⁵	0,00. 10 ⁻⁵
Rate of extraction in %	85	85	84	42	03	00

We noticed that quantitative extractions are obtained for relatively large amounts of salt compared with the Pb²⁺. The minimum amount of salt for quantitative extraction is 25 times greater than that of lead. The amount (in 5 ml) in relation to a liter of solution to give a concentration of 5.10⁻⁴ (mol / l), which is of the same order of magnitude as the salt of CMC (1.25 10⁻⁴ mol / l).

The results obtained show that the extraction begins only above the CMC, which shows that the complexation is lead by the micelles. This was also shown when the complexation of Cu⁺² by sodium dodecylsulfate. The yield of the reaction is related to the fraction of the surfactants present in micelles. It is therefore necessary that the surfactant is at a concentration well above the CMC (approximately 10 times the CMC) in order to obtain sufficient efficacy. The film obtained by the complexation of lead by dithizone constitute an inverse emulsion stabilized by the complex (ethyl bi-décanylmaléiate) Pb.

2. Conclusion

In this work, we performed the synthesis of one of the derivatives alkenilmaleic anhydride, to knowing the ester ethyl bi- decanilmaleiate acid starting from the decene- 1obtenu by dehydration of the decanol in the presence of granulated alumina like catalyst.

The synthesis of this ester was realized in three stages:

- (i) Alkénylation of décène-1 with maleic anhydride following a molar report ½.
- (ii) Esterification of decanilmaleic anhydride with the ethylene glycol.
- (iii) Neutralization of ethyl bi--décanylmaléique acid ester by soda.

The results showed that the product obtained is soluble in water. The carboxylate functions in its structure make it possible for complex metal ions by forming insoluble entities in water. And the complex of lead obtained can be easily separate to aqueous solutions.

The optimal rate of extraction obtained for quantities out of lead concentration $5 \cdot 10^{-5}$ ion g/l and ethyl bi--dècanylmalèiate acid salt of with 10^3 mol/L (8 times higher than its CMC which is about $1.25 \cdot 10^{-4}$ mol/l).

The results show that the extraction starts only beyond the CMC, lead thus is retained by the micelles .This was shown, in addition, at the time complexation of Cu^{2+} with the sodium dodecylsulphate (SDS) or the output of the reaction is related to the fraction of surfactant being in the form of micelles. For a quantitative extraction, it is thus essential that considerable quantities of micelles are present in solution.

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