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

Omar Kaddour, Naima Guettaf, Nadjia Khettab, Abdallah Gherbi

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. 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 chelater 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. 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 installation of heavy metals [7, 8] has led governments to regulate emissions by setting maximum limits. A decree of February 2nd, 1998, related to the installation of heavy metals. One example is the pollutant's 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 in a state of traces. How ever, 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 soils in particular, of heavy metals whose may create significant nuisance.

And this paper deals with the synthesis of the acid salt of bi-ethyl decanylmaléiate 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 decanylmaléique anhydride,
(ii) Esterification reaction of the anhydride découmalélique and ethyleneglycol to obtain bidecanylmaléiate ethyl acid and
(iii) Neutralization reaction of the acid functions of the bi-decanylmaléiate ethyl acid, by caustic soda, to obtain the acid salt bi-decanylmaléiat ethyl which is soluble in water.

1. Material 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 esters obtained in second step with caustic soda.

2. 1.1. Synthesis of anhydride decamélique:

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:

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 decamaléique anhydride

The characteristics of the decamaléique anhydride product by this reaction are shown in Table 2.

2.1.2. Esterification of the decamaléique anhydride and ethyleneglycol:

A. Synthesis of ethyl bi-decamaléiate acid:

Table 1: Decene-1 yield [%]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular Mass</th>
<th>Index of saponification</th>
<th>Active matter yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>238</td>
<td>275.37</td>
<td>58</td>
</tr>
<tr>
<td>II</td>
<td>238</td>
<td>278.70</td>
<td>58.7</td>
</tr>
<tr>
<td>III</td>
<td>238</td>
<td>276.80</td>
<td>58.3</td>
</tr>
</tbody>
</table>

Table 2: Decamaléique anhydride. Characteristics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>molecular Mass</th>
<th>Index of saponification</th>
<th>active matter yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>238</td>
<td>275.37</td>
<td>58</td>
</tr>
<tr>
<td>II</td>
<td>238</td>
<td>278.70</td>
<td>58.7</td>
</tr>
<tr>
<td>III</td>
<td>238</td>
<td>276.80</td>
<td>58.3</td>
</tr>
</tbody>
</table>
The samples obtained are in turn used in the synthesis of the anhydrodecylmaleic derivatives such as esters.

(i) Conducting the experiment:

2 moles of anhydride and decylmaleic, 1 mole ethylene 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 to 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>
<thead>
<tr>
<th>(Reagents + products) esterification</th>
<th>Initial quantities</th>
<th>Final quantities [g]</th>
<th>Product yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>bi-decylmaleic anhydride</td>
<td>58%</td>
<td>96.55</td>
<td>20.27</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>7.52</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>ethyl bi-decylmaleate acid</td>
<td>0.00</td>
<td>114.04</td>
<td></td>
</tr>
</tbody>
</table>

Also we can represent the bi-decylmaleate ethyl acid characteristics in Table 4;

<table>
<thead>
<tr>
<th>esterification product</th>
<th>Performance of active ingredient in %</th>
<th>Acid index</th>
<th>Index of saponification</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl bi-decylmaleate acid</td>
<td>44.82</td>
<td>92.08</td>
<td>91.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>161.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>160.05</td>
</tr>
</tbody>
</table>

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

3.1.3 Neutralization of the bi-decylmaleate 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:

\[
\text{R-CH} = \text{COOCHCH}_2\text{CH}_2\text{OOCC-CH-R} + 2 \text{NaOH} \rightarrow \text{R-CH} = \text{COOCHCH}_2\text{CH}_2\text{OOONa} + \text{NaOOC-CH}_2
\]

<table>
<thead>
<tr>
<th>Table 5: Total field of the neutralization reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid quantity [g]</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>30</td>
</tr>
</tbody>
</table>

2.2. Determination of the critical micelle concentration (CMC) of ethyl bi-decylmaleate 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 aided 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":

\[
\gamma = \frac{F}{2(L+e)} \approx \frac{F}{2L}
\]

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 decaylmaleate vs. Log of C at 20 °C.
The value of the CMC salt obtained was $1.25 \times 10^{-4} \text{ mol/l}$. 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:

<table>
<thead>
<tr>
<th>$\text{Pb}^{2+}$</th>
<th>5.10^{-5}</th>
<th>10^{-4}</th>
<th>5.10^{-6}</th>
<th>10^{-5}</th>
<th>5.10^{-7}</th>
<th>10^{-6}</th>
<th>5.10^{-8}</th>
<th>10^{-7}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorbance</strong></td>
<td>0.070</td>
<td>0.130</td>
<td>0.200</td>
<td>0.260</td>
<td>0.320</td>
<td>0.390</td>
<td>0.525</td>
<td></td>
</tr>
</tbody>
</table>

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

**A. Preparation of samples ethyl bi-decanylmaleate acid salt:**
We have considered a determined volume of each lead solution of a known concentration (5.10^{-4}, 10^{-4}, 5.10^{-5}, 10^{-5}, 5.10^{-6}, 10^{-6}, 5.10^{-7} and 10^{-7} ion g/l ) and we have added the same volume of ethyl bi-decanylmaleate acid salt solubilized in water at a concentration of 5.10^{-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 $[(\text{bi-decanylmaleate ethyl}) \text{ Pb}]$ 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-decanylmaleate acid salt. After separation, the mixture is collected and the filtrate is added 5 ml to the solubilized solution of dithizonein 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 $\text{Pb (DZ)}_2$ 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 decanylmaleiate salt is given by:

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

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 Table 7.

### Table 7: Influence of lead concentration on the extraction rate for a concentration of ethyl bi-decanylmaleate acid salt equal to 5.10^{-3} mol/L

<table>
<thead>
<tr>
<th>Pb^{2+} mol/L</th>
<th>2.5.10^{-3}</th>
<th>5.10^{-3}</th>
<th>2.5.10^{-4}</th>
<th>5.10^{-4}</th>
<th>2.5.10^{-5}</th>
<th>5.10^{-5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of Pb^{2+} with g in 5mL</td>
<td>2.6.10^{-5}</td>
<td>5.2.10^{-7}</td>
<td>2.6.10^{-4}</td>
<td>5.2.10^{-4}</td>
<td>2.5.10^{-4}</td>
<td>5.2.10^{-4}</td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.050</td>
<td>0.070</td>
<td>0.170</td>
<td>0.375</td>
<td>0.225</td>
<td>0.229</td>
</tr>
<tr>
<td>Quantity of Pb^{2+} extracted with dithizone</td>
<td>2.6.10^{-7}</td>
<td>5.2.10^{-7}</td>
<td>2.04.10^{-4}</td>
<td>2.2.10^{-4}</td>
<td>0.45.10^{-5}</td>
<td>0.8.10^{-5}</td>
</tr>
<tr>
<td>Quantity of Pb^{2+} extracted with ethyl bi-decanylmaleate acid salt</td>
<td>0.000</td>
<td>0.000</td>
<td>0.56.10^{-4}</td>
<td>3.00.10^{-4}</td>
<td>2.00.10^{-4}</td>
<td>4.40.10^{-4}</td>
</tr>
<tr>
<td>Extraction rate</td>
<td>0%</td>
<td>0%</td>
<td>21%</td>
<td>58%</td>
<td>82%</td>
<td>85%</td>
</tr>
</tbody>
</table>

We noticed that quantitative extractions are obtained for relatively large amounts of salt compared with the Pb^{2+}. 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-decanylmaleate) Pb.

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

<table>
<thead>
<tr>
<th>m [bi-ethyl decanylmaleate acid salt] mol/l</th>
<th>2.5.10^{-3}</th>
<th>5.10^{-3}</th>
<th>5.10^{-4}</th>
<th>2.5.10^{-4}</th>
<th>5.10^{-5}</th>
<th>2.5.10^{-5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>m Pb^{2+} (g) before extraction in 5ml of solution</td>
<td>5.2.10^{-4}</td>
<td>5.2.10^{-4}</td>
<td>5.2.10^{-4}</td>
<td>5.2.10^{-4}</td>
<td>5.2.10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Pb^{2+} (g) extracted with dithizone</td>
<td>0.8.10^{-5}</td>
<td>0.8.10^{-5}</td>
<td>0.8.10^{-5}</td>
<td>3.10^{-5}</td>
<td>5.05.10^{-5}</td>
<td>5.2.10^{-5}</td>
</tr>
<tr>
<td>Rate of extraction in %</td>
<td>85</td>
<td>85</td>
<td>84</td>
<td>42</td>
<td>63</td>
<td>00</td>
</tr>
</tbody>
</table>

We noticed that quantitative extractions are obtained for relatively large amounts of salt compared with the Pb^{2+}. 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).

### Conclusion

In this work, we performed the synthesis of one of the derivatives alkenylmaleic anhydride, to knowing the ester ethyl bi-decanylmaleate 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 ¼.

(ii) Esterification of decanoyl maleic anhydride with the ethylene glycol.

(iii) Neutralization of ethyl bi–décanylmaleique 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 $5 \times 10^{-5}$ ion g/l and ethyl bi–décanylnaléiate acid salt of with $10^{-3}$ mol/L (8 times higher than its CMC which is about $1.25 \times 10^{-4}$ 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 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.

References:


[11] FARMER E.H ,Certaine fudbamental concepts relatng to non polar mecha-