Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/17056
DOI URL: http://dx.doi.org/10.21474/IJAR01/17056

RESEARCH ARTICLE

Double solubility of kerogen and carbonates from Tarfaya oil shale (Morocco) by potable water, distilled water or seawater from the Atlantic Ocean

Amina Aitlahcen, Asmaa Khaya and Abdeljabbar Attaoui
Department of Chemistry, Faculty of Sciences Ben m''sik Casablanca, University Hassan II Morocco.

Manuscript Info

Manuscript History
Received: 05 April 2023
Final Accepted: 10 May 2023
Published: June 2023

Abstract

The solubility of the materials contained in oil shale has often been questioned. Ordinary water coming directly from purification stations or partially distilled water are of primary interest in the energy industry for exploitation or research. Similarly, given that a large proportion of the Tarfaya oil shale is immersed in the Atlantic Ocean, we thought it would be interesting to study the effect of these types of water on the solubility of kerogen under physical conditions of moderate temperature. Ultra-violet and infra-red spectroscopy was used in this work. As the identification energy of the ultraviolet is fairly high compared with the infrared and visible. We were able to follow the evolution of heavy matter from kerogen. The effect of temperature was also highlighted. Spectroscopic identification uses radiation of varying energies depending on the compounds to be detected. For example, for infrared, the energy used to identify substituted unsaturated aliphatic is higher than that used to identify substituted unsaturated monocyclic. As far as our work is concerned, the energy used for identification by UV is sufficiently higher than that for infrared, which means that the compounds to be detected from oil shale can only be heavy hydrocarbons (branched and multisubstituted unsaturated aliphatic chains). Similarly, supercritical fluid extraction using water and other solvents such as toluene is often used to determine the different fractions of organic compounds in oil shale. We are going to use three analytical methods to highlight this solubility in seawater (subsequently the solubility in distilled water), which are ultra-violet spectroscopy, infra-red spectroscopy and the determination of carbonates (mineral matter) by complexometry.

Introduction:-

Supercritical fluid extraction methods use water and toluene as solvents, in this work we will try to find out the effect of solvating water, more precisely seawater (Atlantic Ocean) under moderate physical conditions. There are two main classes of solvents: protic solvents, in which certain hydrogen atoms are bonded to a heteroatom such as O or N. These solvents are capable of forming hydrogen bonds or protonating anions, and are highly ionizing; and aprotic solvents, in which all the hydrogen are bonded to carbon atoms. They are divided into two categories a polar aprotic solvent, which are solvents incapable of making hydrogen bonds. They are therefore not very ionizing and are not very solvent, and polar aprotic solvents are generally very strong solvents. They are used when low-polarity

Corresponding Author:- Abdeljabbar Attaoui
Address:- Department of Chemistry, Faculty of Sciences Ben m''sik Casablanca, University Hassan II Morocco.

organic compounds need to be reacted with polar reagents or when anionic nucleophiles need to be generated. These solvents are poor solvates for anions, but very good solvates for cations.

We cite the work done by the authors **(T.Fanazukuri et al: 1988)** who studied Chinese oil shale from Maoming which were subjected to supercritical fluid extraction (SFE) with water and toluene separately. Oils with similar hydrogen distributions were obtained from SFE and pyrolysis (when heated from room temperature to 673°K and cooled immediately, in both SFE and pyrolysis). Extraction was carried out by Soxhlet. Under supercritical conditions, it was found that the polar components were more easily decomposed with water than with toluene. The yield of non-polar components was not affected by the solvent, water or toluene.

1/ Literature Review:-

Considerable attention has been paid to the use of water in the supercritical fluid extraction (SFE) of organic matter from fossil fuels. The authors **(G.V.Deshpande et al: 1984)** discovered that supercritical water acts not only as a solvent but also as a reagent in the conversion of coal to gas and liquid. The authors **(T.J.Houser et al: 1986)** also found that supercritical water (SC) plays an active role in the decomposition of organic compounds. Compared with the considerable amount of work carried out on coal ETS, little has been done on oil shale ETS. The authors **(K.Z.Qin et al: 1984, Y.Zhu: 1982)** studied the ETS of Chinese oil shale with toluene. The company **(Standarrd Oil Company, Indiana, USA: 1978)** patented a process for recovering upgraded hydrocarbons extracted from oil shale using SC water and a mixture of SC water, hydrogen and catalysts. The authors **(J.FMcKay et al: 1983)** studied SF extraction from Green River oil shale using water and a mixture of water and various organic solvents, and found a mixture of water and methanol to be effective for extraction.

The authors **(T.Funazukuri et al: 1988)** studied the extraction of oil from oil shale in a batch autoclave at a heating rate of 8.5°K min-1, from ambient to 673°K for one hour either in an atmosphere of water, argon and CO or in an atmosphere of water, CO and Na_2CO_3. The total yield obtained is slightly higher with water and CO than with water, CO and Na_2CO_3. As examined by authors **(H.H.Oelert et al: 1976, P.Bjornbom et al: 1987)**, attention has been paid since other authors **(F.Fisher et al: 1921)** to the hydrogenated liquefaction of carbonaceous materials by the water gas shift reaction (WGSR) in an atmosphere of steam and CO or synthesized gas of CO + H_2. It has been found that the presence of CO or H_2 during liquefaction suppresses the recombination of depolymerized fragments, and the hydrogen produced from the WGSR stabilizes the fragments.In hydrogenated liquefaction, various types of catalyst, such as basic salts **(D.S.Ross et al: 1984**), alkaline carbonates **(J.C.Cavalier et al: 1978)**, alkaline hydroxides **(D.S.Ross and J.E.Blessing: 1978)** and solid catalysts **(Y.Takemura and K.Ouchi : 1983)** have been tested. In addition, the addition of carbon monoxide to steam as a solvent in the absence of catalysts has proved effective in increasing oil yields **(J.M.L.Penninger: 1985)** and increasing the conversion of carbonaceous materials. The authors **(J.C .Cavalier and E.Chornet: 1977)** emphasized that liquefaction using water and CO played an important role in improving the transfer of hydrogen and the dissolution of organic substances. Authors **(Y.Takemura and K.Ouchi: 1983)** discovered that in coal liquefaction in water and CO, the presence of these solvents lowered the WGSR reaction rate, but increased the coal conversion rate. Authors **(L.A.Amestica and E.E.Wolf: 1986)** carried out the catalytic liquefaction of coal with supercritical water and CO in the absence or presence of the organic solvents tetrahydroquinoline, tetralin and toluene. They found that the addition of organic solvent increased the yield of the toluene-soluble fraction and that under supercritical conditions the solubility and diffusivity of the solvent became high and reduced the resistance to mass transfer.

Some studies on the hydrogenated treatment of oil shale under supercritical conditions enabled the authors **(R.M.Balduin and K.W.Chen: 1987)** to study the pyrolysis of supercritical toluene, hydrogen and tetralin.

2/ Objective and study of the problem presented:-

The solubility of oil shale has often been approached in an attempt to study the raw material. The aim is to describe oil shale, either to classify it and determine the size of the deposit in question, or to extract its constituents and exploit them in various industries.

The solvents used are either a polar aprotic or polar solvents (the hydrogen atoms are bonded to carbon atoms) or potic solvents (the hydrogen atoms are bonded to a heteroatom such as O or N). The most commonly used solvents are chloroform ($HCCl_3$), which is used to crack organic matter and classify it for the different layers of the deposit under consideration, and to predict the existence of the phenomenon in situ **(Ahmed Malal, Doha Lahmadi and**

AbdeljabbarAttaoui: 2022). We also mention toluene solubility for extracting organic compounds for exploitation. We also mention the solvent ethane tetrachloride (1, 1, 1) to quantitatively classify aliphatic compounds and preventive compounds in oil shale **(A.Farah,N.Azouaz and A.Attaoui et al 2022).**

The solubility by water is often mentioned, in this work we are going to follow this solubility for three types of water in physical conditions of moderate temperatures, these types of water are the drinking water of the city of Casablanca, the distilled water and the sea water of the Atlantic Ocean.

3/ Experimental study:

The experimental techniques used are spectroscopy at different energies. A low absorption energy is the case of infra-red spectroscopy, used for the solubility of water in the Atlantic Ocean. Then high absorption energy, as in the case of ultra-violet spectroscopy, used to determine solubility in drinking water or distilled water. We also carried out complexometric assays to monitor Ca2+, which is the main element in oil shale.

4/ Use of potable water (Casablanca) as a solvent.

4.1: Preparation of samples:

We prepared seven solutions containing 1g of crushed shale (Z1 layer) in 50 cm^3 of tap water. After heating for 10 minutes, the solutions were left to settle for 3 minutes, and then filtered into test tubes.

4.2: Analysis by UV spectroscopy:

After preparing the samples, we proceeded to analysis using the Ultra-Violet spectroscopic method (in the analysis room at the BEN M'SIK faculty), and we obtained peaks A (absorbance) = f (λ).

The spectra in the following figures (figure 5, figure 6, figure 7, figure 8, figure 9, figure 10 and figure 11) represent the Ultra-violet identification of the resulting solute after filtration at temperatures of 19, 34, 48, 64, 74, 84 and 100 0C respectively:

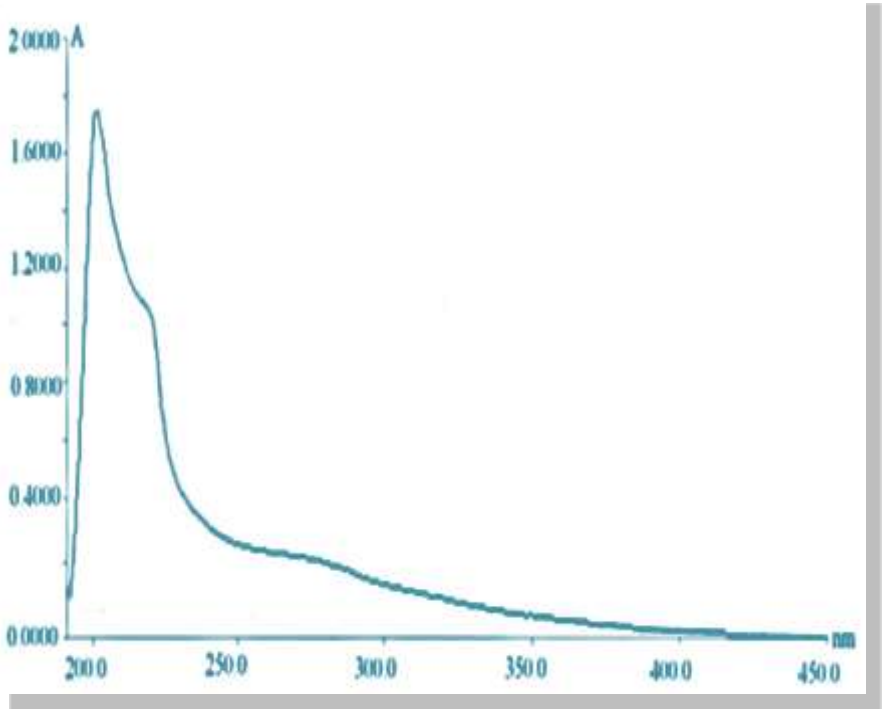

Fig5:-UV spectrum of the solute.

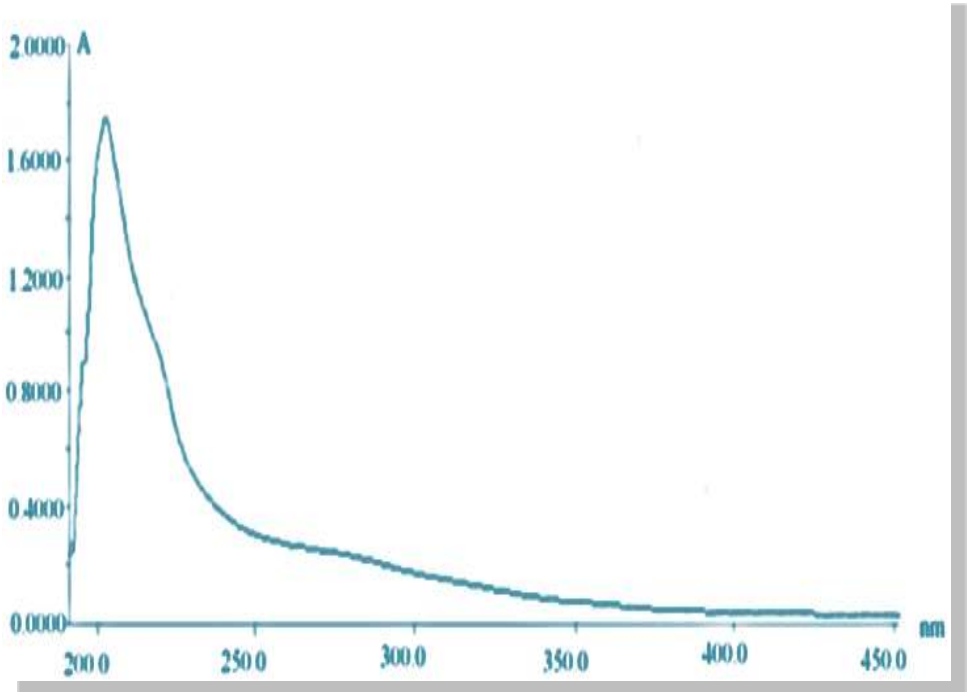

Fig 6:- UV spectrum of solute after after filtration of one gram of shale (Z1) filtration of one gram of shale (Z1)solubilized by 50 cm^3 of potable solubilized by cm3 of potable waterwater at a temperature of 19°C. at a temperature of 34°C.

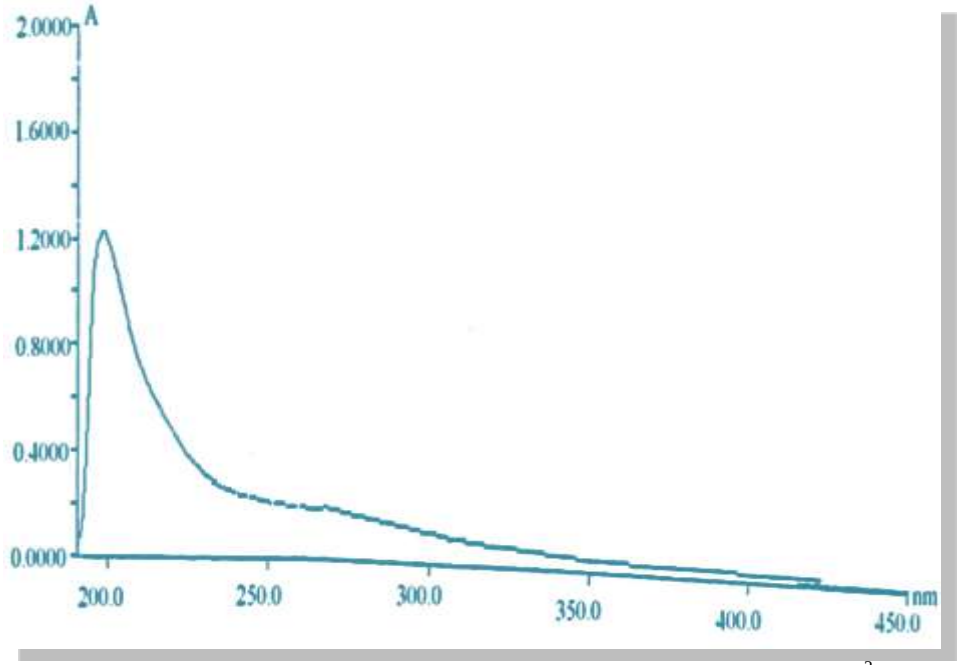

Fig7:-UV spectrum of the soluteafter filtration of one gram of shale (Z1)solubilized by 50 cm^3 of potablewater at a temperature of 48°C.at a temperature of 64°C.

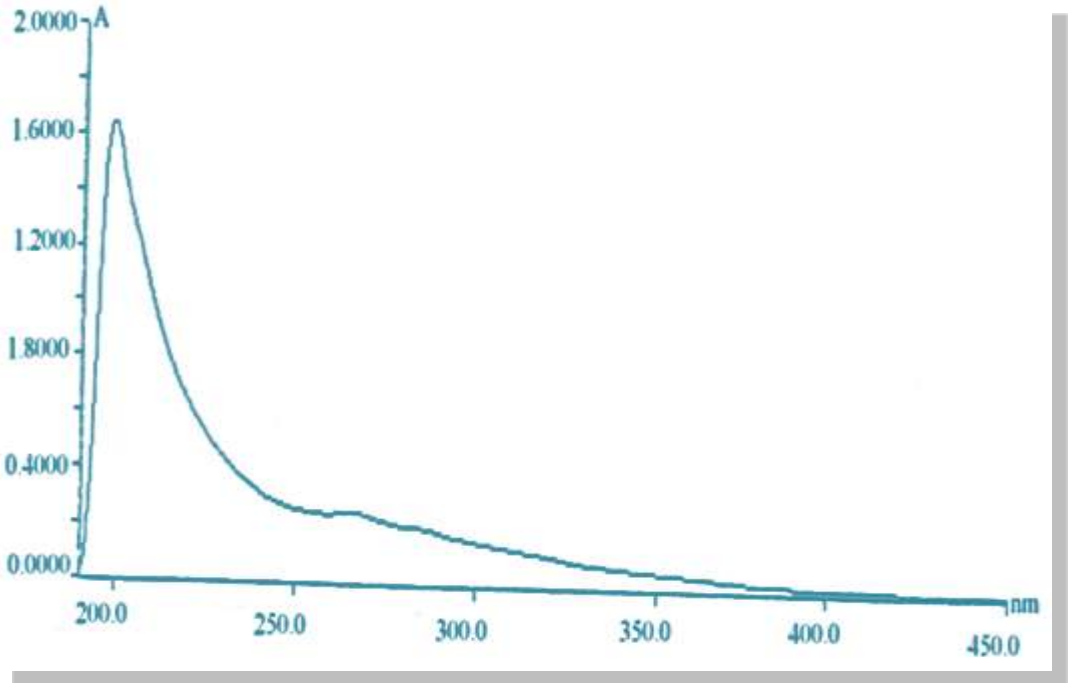

Fig 8:- UV spectrum of solute afterfiltration of one gram of shale (Z1)solubilized by cm3 of potable water.

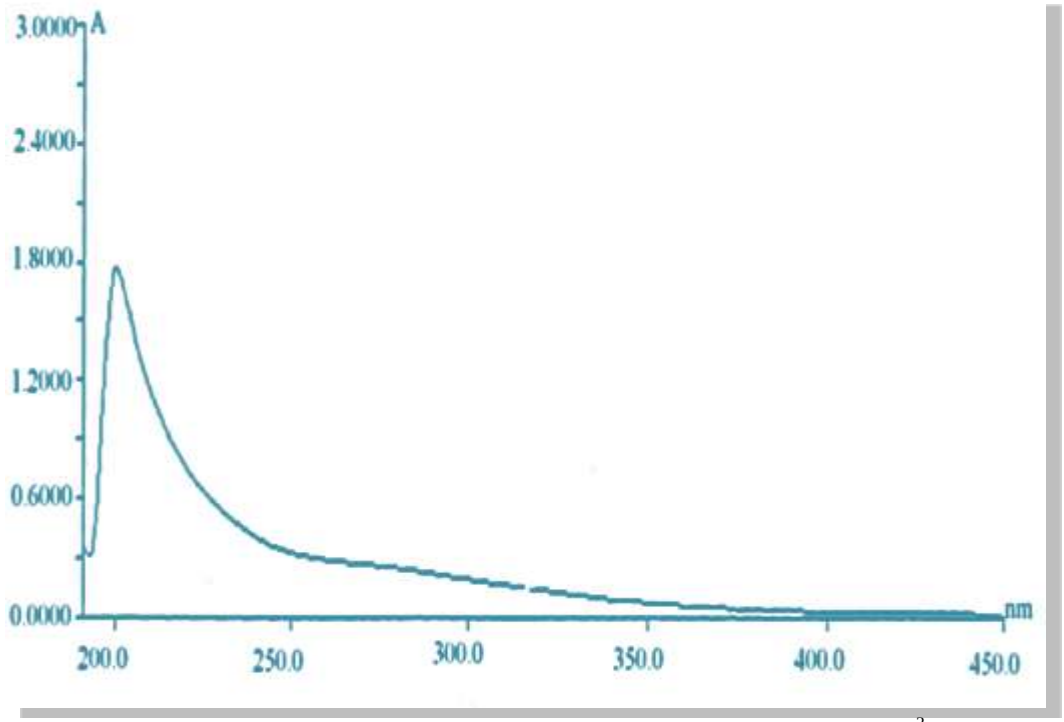

Fig9:-UV spectrum of the soluteafter filtration of one gram of shale (Z1)solubilized by 50 cm^3 of potablewater at a temperature of 74°C.at a temperature of 84°C.

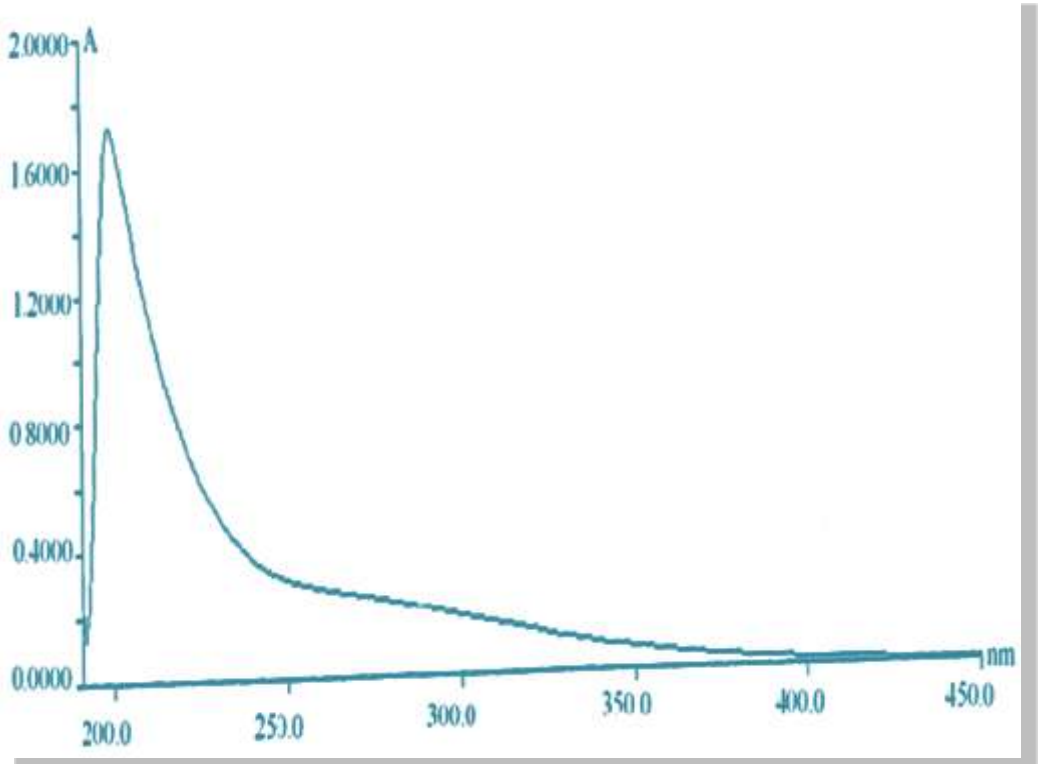

Fig 10:- UV spectrum of solute afterfiltration of one gram of shale (Z1)solubilized by cm3 of potable water.

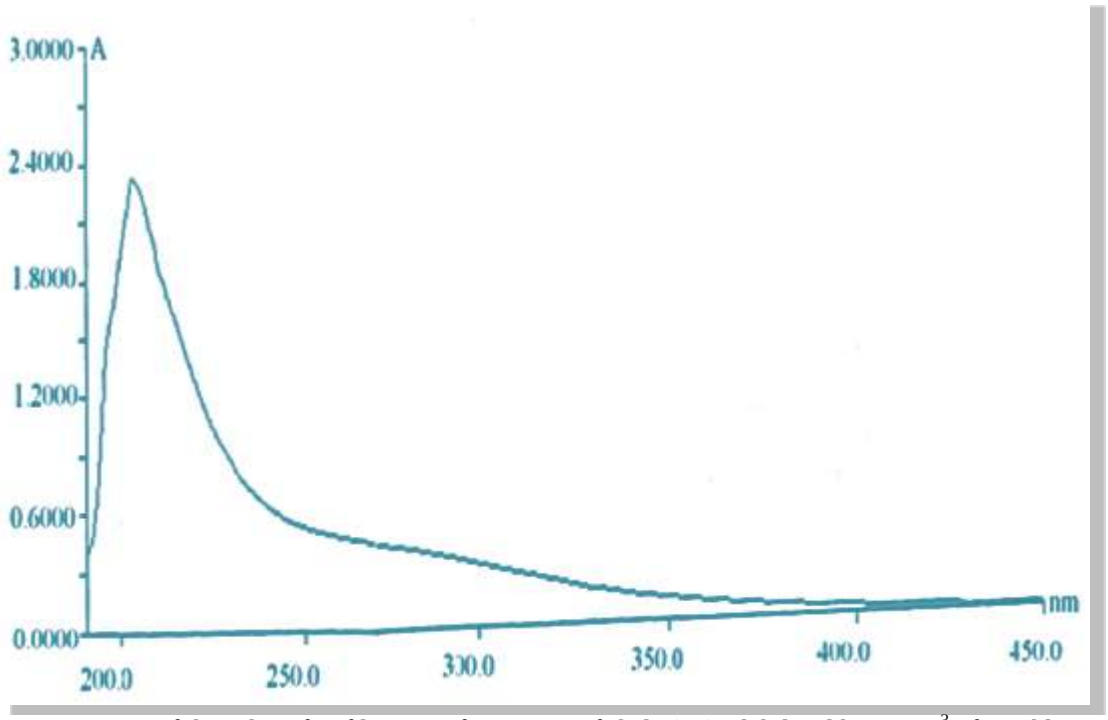

Fig11:-UV spectrum of the soluteafter filtration of one gram of shale (Z1)solubilized by 50 cm^3 of potablewater at a temperature of 100°C.

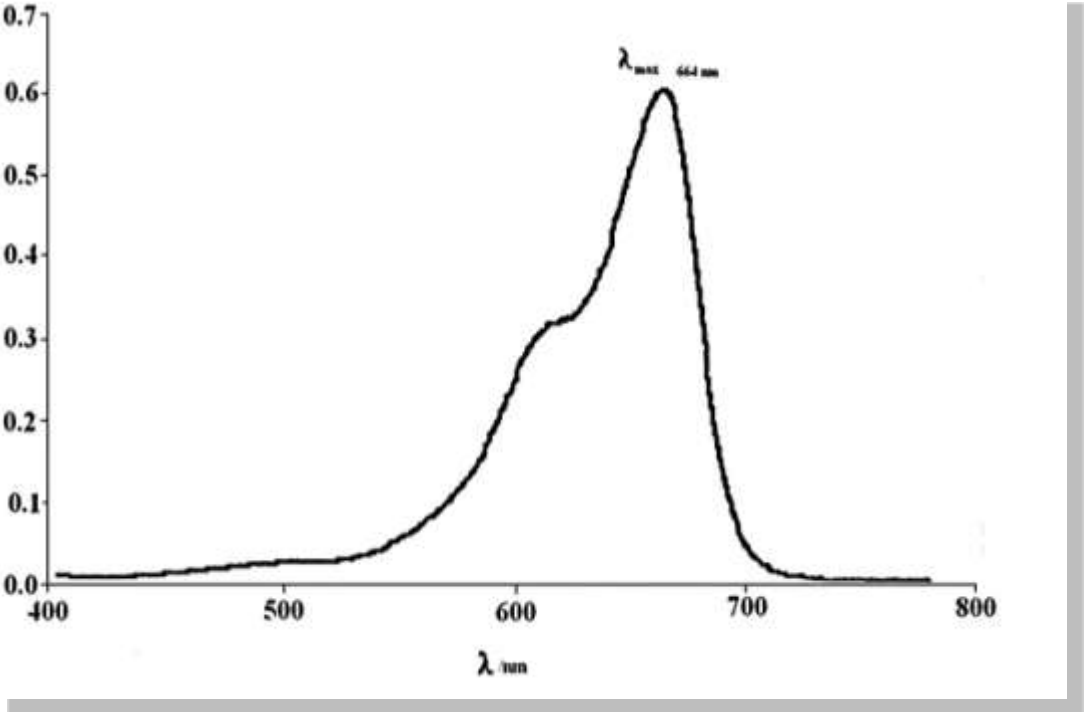

Fig 12:- Visible UV of methylene blueuses the PERKINE apparatus.

For the calibration and by applying Beer-Lambert's law A=IεC we chose methylene blue (purity 95%, solubility in water at 25°C=40 g/l and molar mass=319.86 g/mole from which C=0.119 mole/l) (figure 12).

This led us to calculate the Iε factor for the apparatus, which is of the order of 5.04A.l/mole.

By identifying and calculating the concentrations, we have compiled the results in Table 1 below:

Table 1:-UV analysis of different shale samples solubilized at different temperatures by potable water.

Temperature (^{0}C)	Absorbance	Wavelength	Concentration (mole/liter)
19	1.7333	202.4	0.3439
34	1.7333	200	0.3439
48	1.2222	198.68	0.2425
64	1.6444	198.68	0.3263
74	1.7666	200	0.3505
84	1.7111	198.69	0.3395
100	2.3333	265.79	0.4630

4.3; Exploitation of results

Solubility of Tarfaya oil shale by potable water is noticeable even at room temperature. Ultraviolet spectra at this wavelength (~ 200 nm) show absorbance for aliphatic, unsaturated and multisubstituted chains (see the complexity of the kerogen molecule). At a temperature of 48°C we observe a decrease in absorbance, which can only be explained by the fact that at this temperature the material decomposes by reorganizing the aliphatic, unsaturated and multisubstituted hydrocarbons, releasing light hydrocarbon compounds, and the aliphatic, unsaturated and multisubstituted chains become heavier. After this temperature, with a few fluctuations, it is clear that the phenomenon of solubility obeys thermal laws, with solubility increasing as a function of temperature.

5/ Use of distilled water as a solvent:

5.1: Sample preparation and analysis:

The same treatments as above were carried out for the Tarfaya shale (Z1), this time using distilled water as the solvent. The spectra in the following figures (Figure 13, Figure 14, Figure 15, Figure 16, Figure 17, Figure 18 and Figure 19) represent the ultra-violet spectroscopy after treatment of the samples at different temperatures.

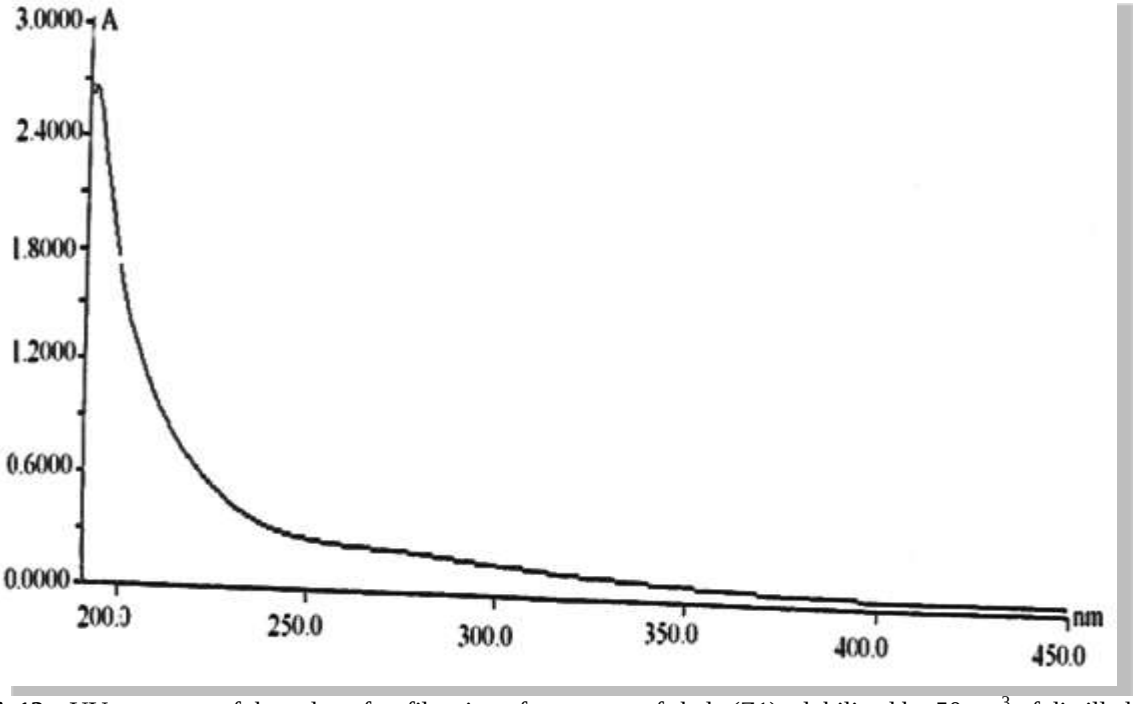

Fig13:- UV spectrum of the soluteafter filtration of one gram of shale (Z1)solubilized by 50 cm^3 of distilled.

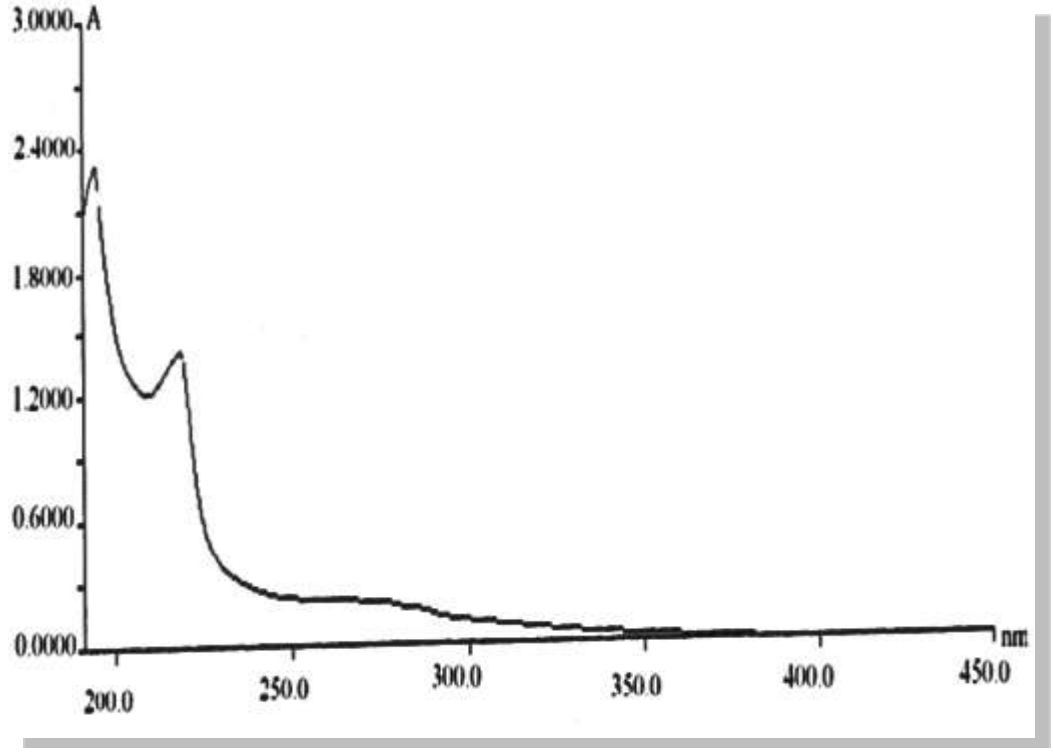

Fig 14:- UV spectrum of solute afterfiltration of one gram of shale (Z1)solubilized by cm3 of distilled water.

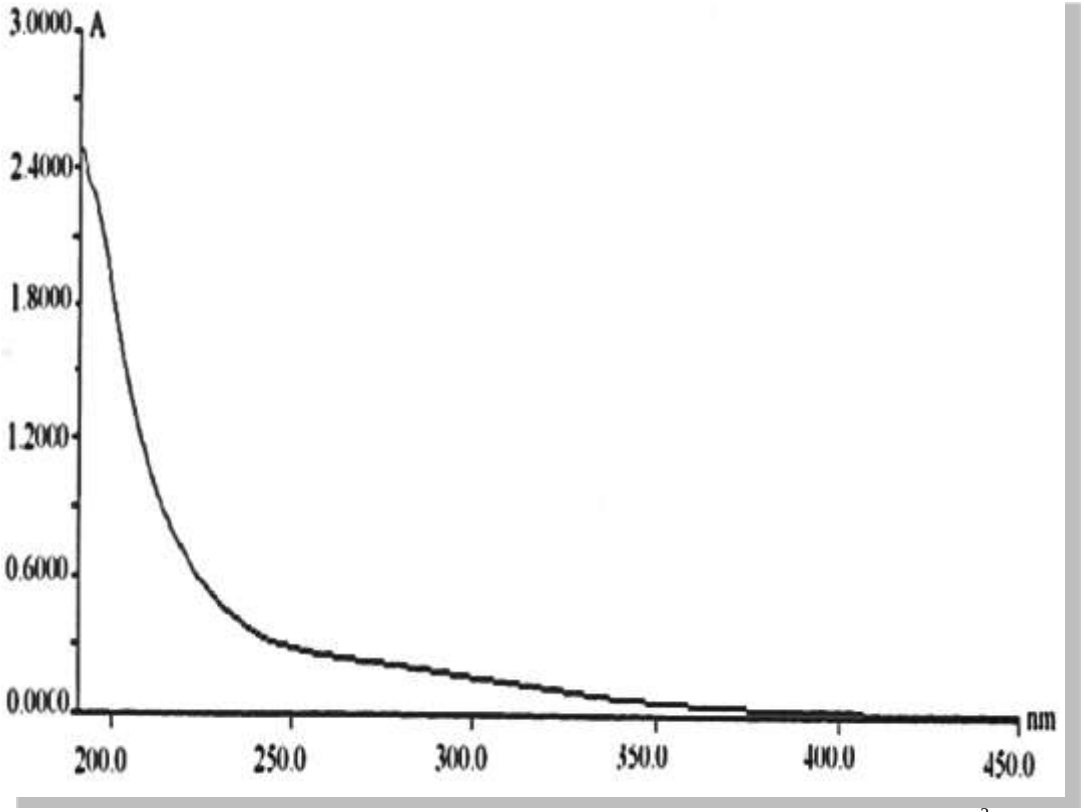

Fig15:- UV spectrum of the soluteafter filtration of one gram of shale (Z1)solubilized by 50 cm^3 of distilled.

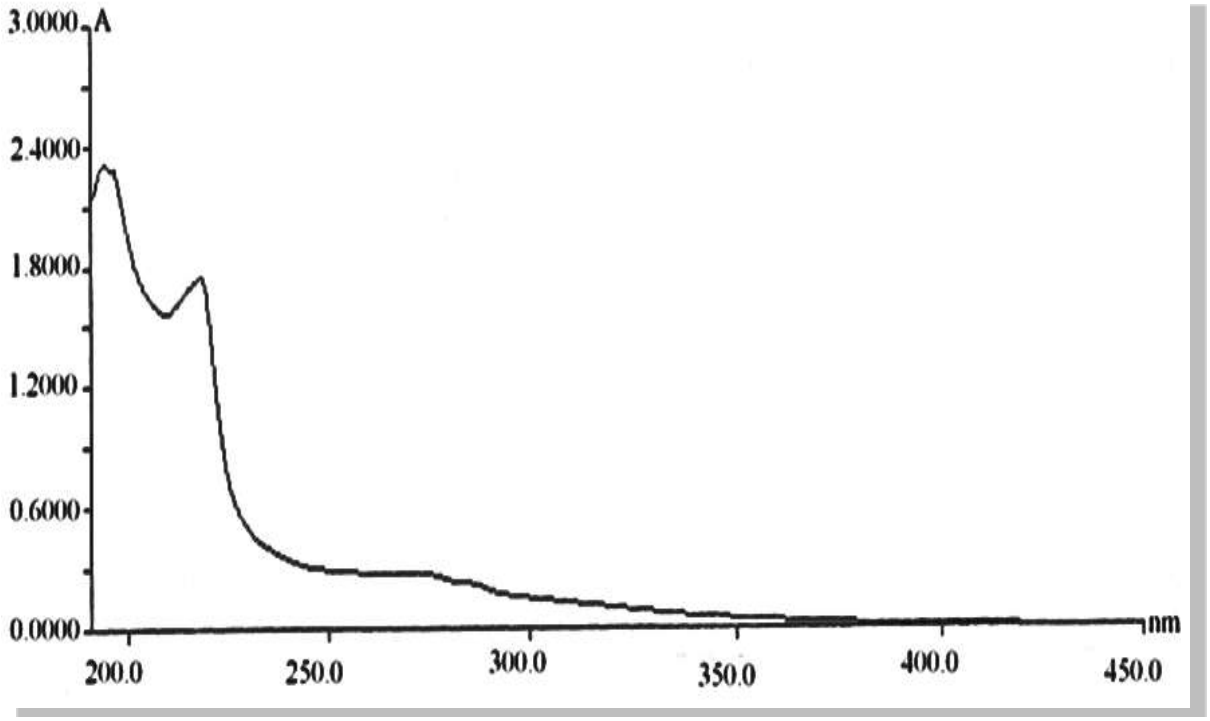

Fig 16:- UV spectrum of solute after filtration of one gram of shale (Z1)solubilized by cm3 of distilled water.

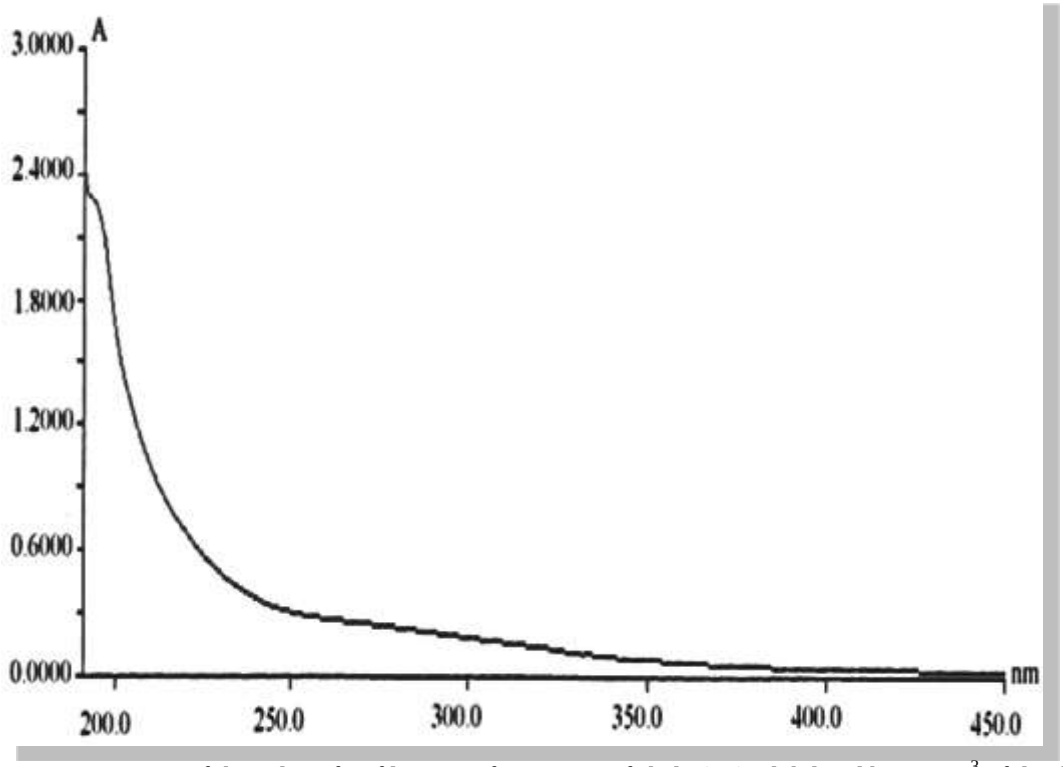

Fig17:- UV spectrum of the soluteafter filtration of one gram of shale (Z1)solubilized by 50 cm^3 of distilled.

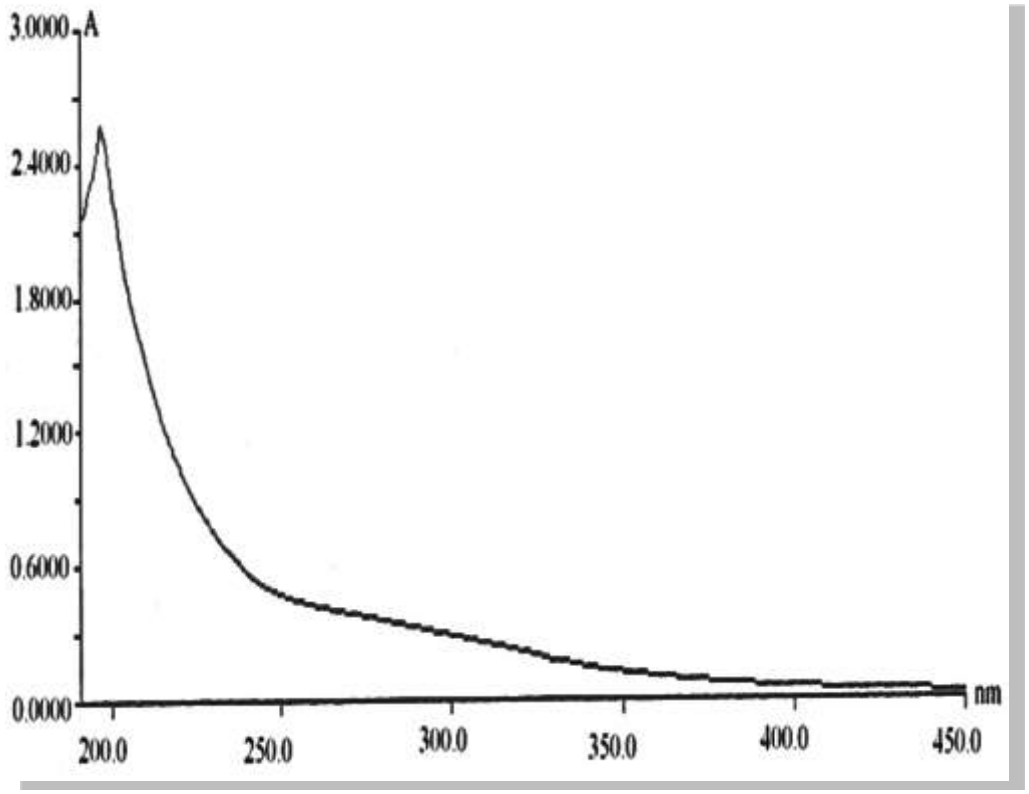

Fig 18:- UV spectrum of solute afterfiltration of one gram of shale (Z1)solubilized by cm3 of distilled water.

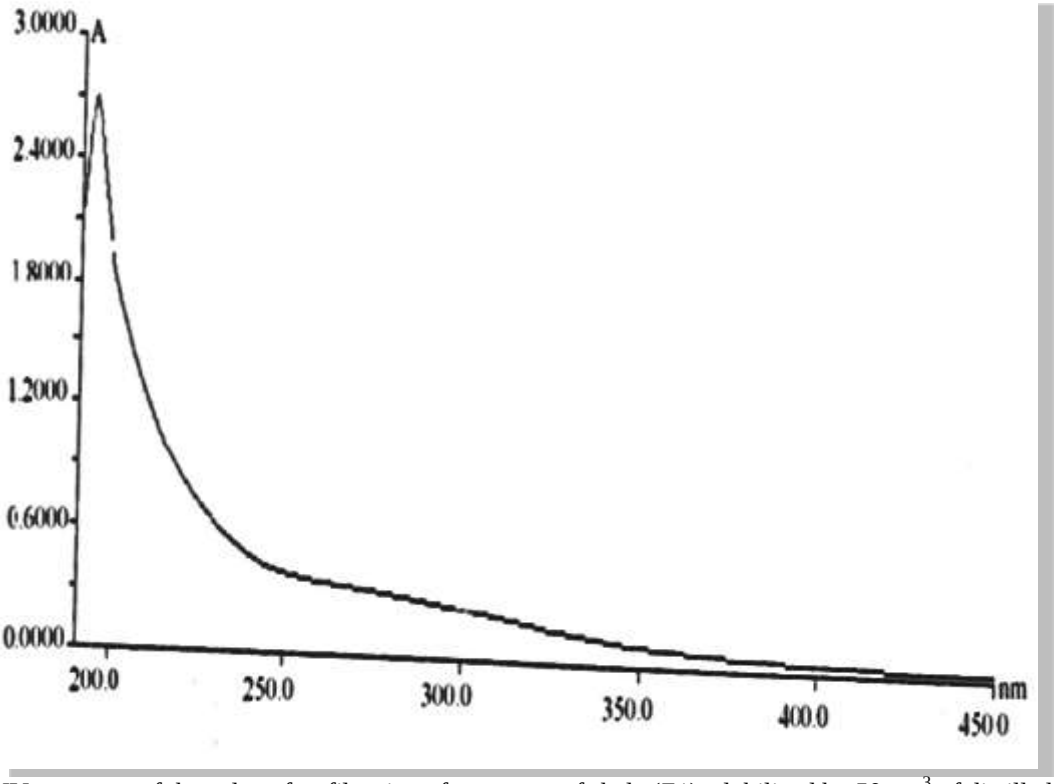

Fig20:- UV spectrum of the soluteafter filtration of one gram of shale (Z1)solubilized by 50 cm^3 of distilledwater at a temperature of 98°C.

The table below shows the absorbance, wavelengths and concentrations obtained after using the factor Iε= 5.04 A.l/Mole of the apparatus.

Table 2:- UV analysis of different shale samples solubilized at different temperatures by distilled water.

Temperature (^{0}C)	Absorbance	Wavelength	Concentration (mole/liter)
20	2.6666	193.42	0.5291
40	2.3000	193.42	0.4563
	1.4000	218.42	0.2778
48	2.4666	190.79	0.4894
59	2.3000	194.74	0.4563
	1.7333	217.10	0.3439
72	2.4000	190.79	0.4762
86	2.5666	194.74	0.5092
98	2.7000	193.42	0.5357

5.3: Results:-

The first observation is that distilled water conducts heat more easily at the first chosen temperatures than when tap water is used. Indeed, at the same voltage, we observed much higher temperatures for distilled water as a solvent (at 20 0C and 40 0C), and solubility is also accentuated when distilled water is used, given the higher concentration. A drop in absorbance was observed at 48 0C, corresponding to a departure of light matter and reorganization of the aliphatic, unsaturated and multisubstituted chains as they became heavier. A multiplicity of peaks at temperatures of 40 0C and 59 0C is observed due to the appearance of two types of aliphatic, unsaturated and multisubstituted materials, one of which is lighter and less concentrated than the other. Lastly, the solubility deduced at temperatures above 72 0C to 98 0C is consistent with thermal laws.

6/ Using water from the Atlantic Ocean as a solvent:

6.1: Experimental techniques

This part of the study uses two analytical methods. The first involves volumetric measurements by complexometry of the solute part, followed by a second Fourier transform infrared spectroscopic method for the precipitate, enabling a qualitative and quantitative study of the light hydrocarbons. It should be noted thatlight hydrocarbons in oil shale are unsaturated aliphatic chains with high identification energy and aromatic chains with low energy.

6.1.1; Complexometric determination.

A simple reaction was the subject of this technique, which consists of complexometric determination using the complexing agent EDTA (ethylene diamine tetra acetic acid):

$M^{2+} + H_2Y^{2-} \rightarrow MY^{2-} + 2H^+$

M^{2+} (Ca^{2+}, Mg^{2+}, Na^+ ...)

The reaction takes place in a PH=10 environment to avoid precipitation of the metal hydroxides. The indicator for this reaction is eriochrome black (NET).

6.1.2: Infrared spectroscopic analysis.

In an infrared spectrometer, a beam of infrared light is produced and split into two beams. One passes through the sample, the other through a reference, which is sometimes the compound in which the sample has been dissolved. The beams are then reflected back to a detector, after passing through a splitter that rapidly alternates the beams entering the detector. The two signals are compared and the resulting spectrum plotted.

6.2: Experimental results.

As is well known, oil shale have a mineral matrix containing a large proportion of carbonates, in the form of calcite (CaCO3) and dolomite ($MgCa(CO_3)_2$), and seawater also contains sodium Na^+. It seemed obvious to us to measure these cations (Ca^{2+}, Mg^{2+} and Na^+) using complexometry.

6.2.1: Complexometric determination of mineral matter.

Samples of oil shale from the Z0 layer (surface layer) and Z4 layer (deep layer) weighing around 2 grams were solubilized in 50 cm3 of Atlantic Ocean seawater with constant stirring for 15 minutes at various moderate temperatures. The mixture thus formed was left to settle for 5 minutes, after which it was filtered through a funnel using filtration paper. The filtrate was then assayed with EDTA (0.052 mole/liter) and the precipitate analyzed by IR. In the following table we have put together the volumes of the assay under the same conditions at the different temperatures mentioned, as well as the volume of the assay of 10 cm3 of seawater alone, in order to make the difference and work out the quantity of cation in the oil shale carbonates solubilized by the seawater.

Table 3:- Complexometric dosage.

Samples	Dosage volume (cm^3)	T(°C)	Ca^{2+} and Mg^{2+} concentration (mol/l)
Sea water	13,4	ambient	-
Z0	15	ambient	$8\ 10^{-3}$
Z0	15,2	24,5	$9\ 10^{-3}$
Z0	14,9	39,5	$7\ 10^{-3}$
Z0	15,2	49	$9\ 10^{-3}$
Z4	14,4	ambient	$5\ 10^{-3}$
Z4	14,1	24,5	$3\ 10^{-3}$
Z4	14,45	49	$5\ 10^{-3}$
Z4	14,4	52	$5\ 10^{-3}$

Initially, the results in the table show that the carbonate concentration is higher in the Z0 layer than in the Z4 layer, which confirms the thermogravimetric data **(A.Attaoui et al: 2022)**. Similarly, up to the maximum temperature (52°C) of our study, the same element concentrations are repeated, so up to 50°C, the maximum natural temperature, solubility is insensitive to this effect.

Seawater contains sodium Na^+ due to carbonate cations and sodium $Na^{+,}$ so under the same conditions, we treated the two layers Z0 and Z4 with distilled water to find out the difference.

Samples	Dosage volume (cm^3)	T (°C)	Ca^{2+} and Mg^{2+} concentration (mole/l)
Z0	1,3	ambient	$7\ 10^{-3}$
Z4	1	ambient	$5\ 10^{-3}$

6.2.2: Infrared spectroscopy identifying the organic matter.

The previously prepared precipitate was analysed by solid state IR in a KBr matrix. The following spectra represent this analysis.

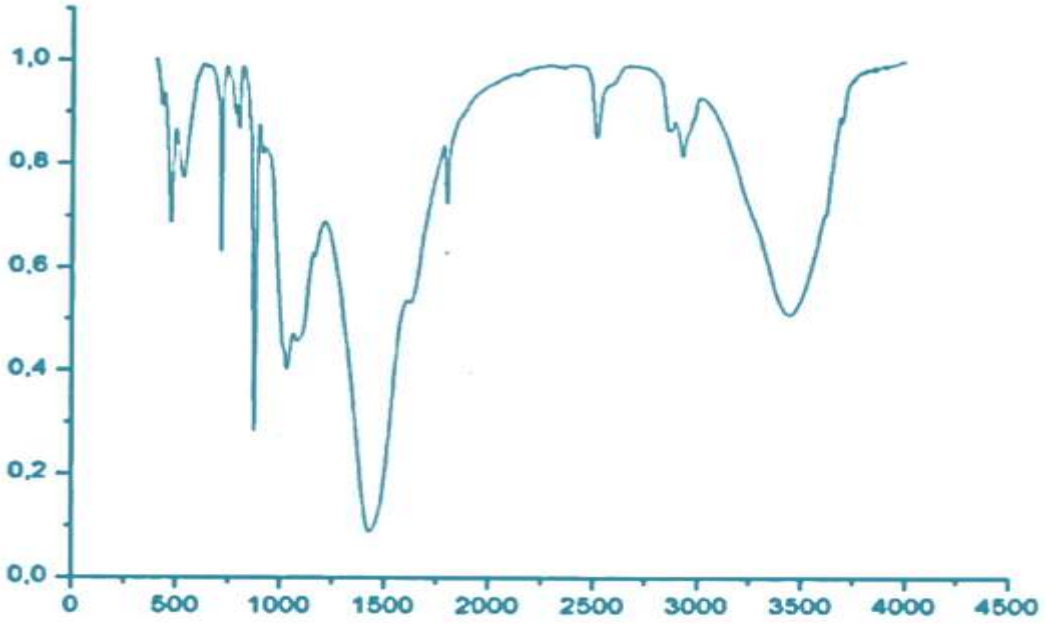

Fig 21:- IR spectrum of the precipitate after filtration of one gram of shale (Z0) solubilized by 50 cm^3 of ocean water at ambient temperature 21°C.

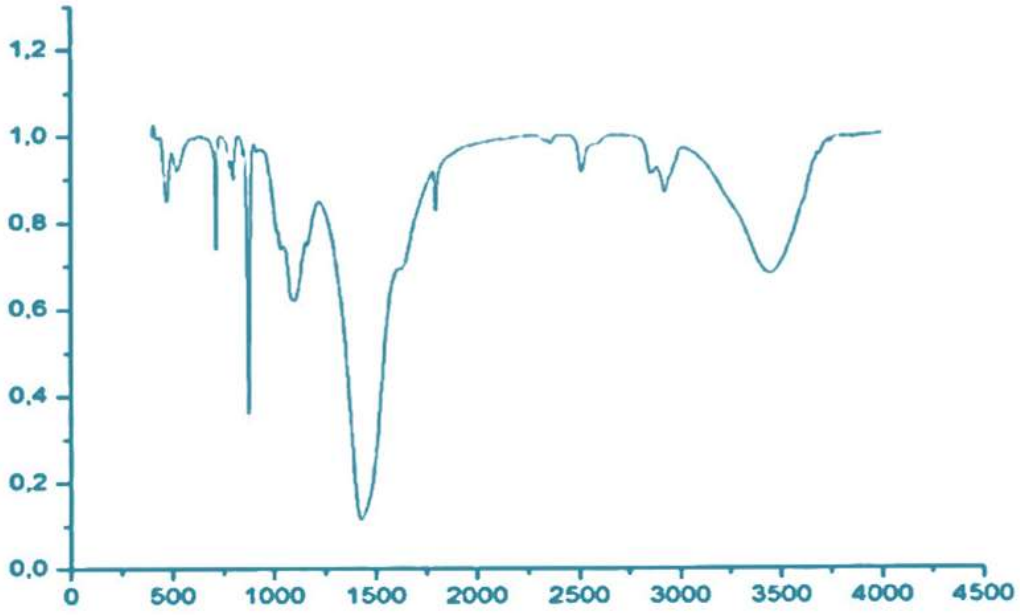

Fig 22:- IR spectrum of the precipitate after filtration of one gram of shale (Z0) solubilized by 50 cm^3 of ocean water at ambient temperature 27, 5°C.

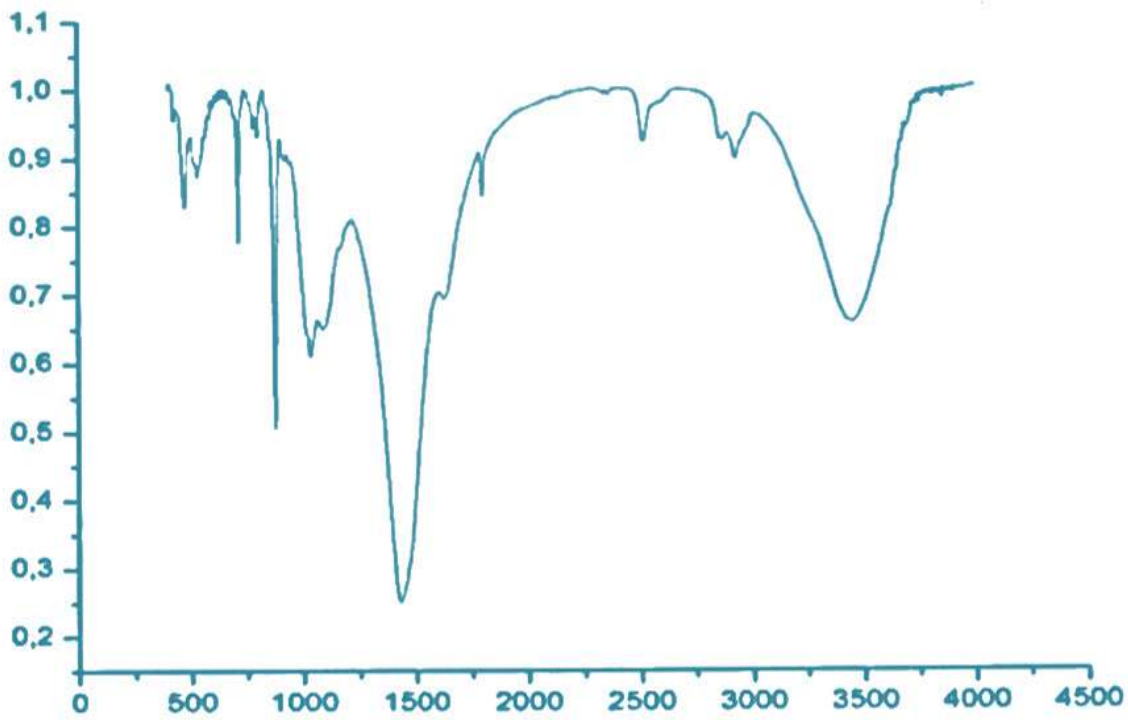

Fig 23:- IR spectrum of the precipitate after filtration of one gram of shale (Z0) solubilized by 50 cm^3 of ocean water at ambient temperature 49°C.

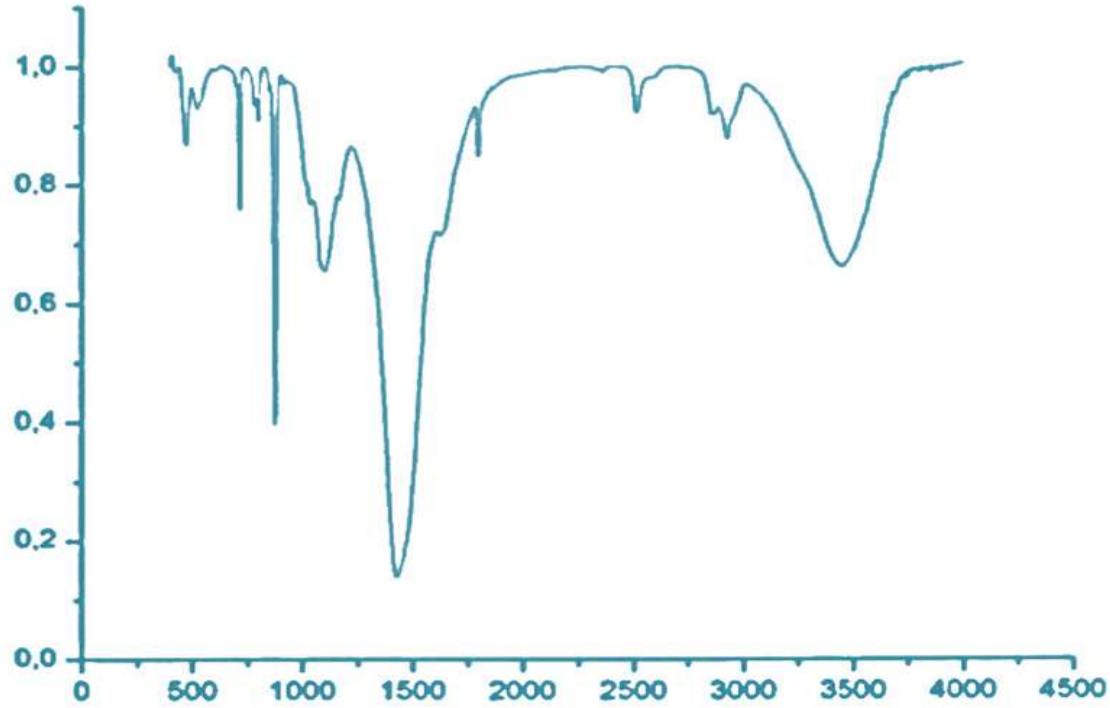

Fig 24:- IR spectrum of the precipitate after filtration of one gram of shale (Z4) solubilized by 50 cm^3 of ocean water at ambient temperature 21°C.

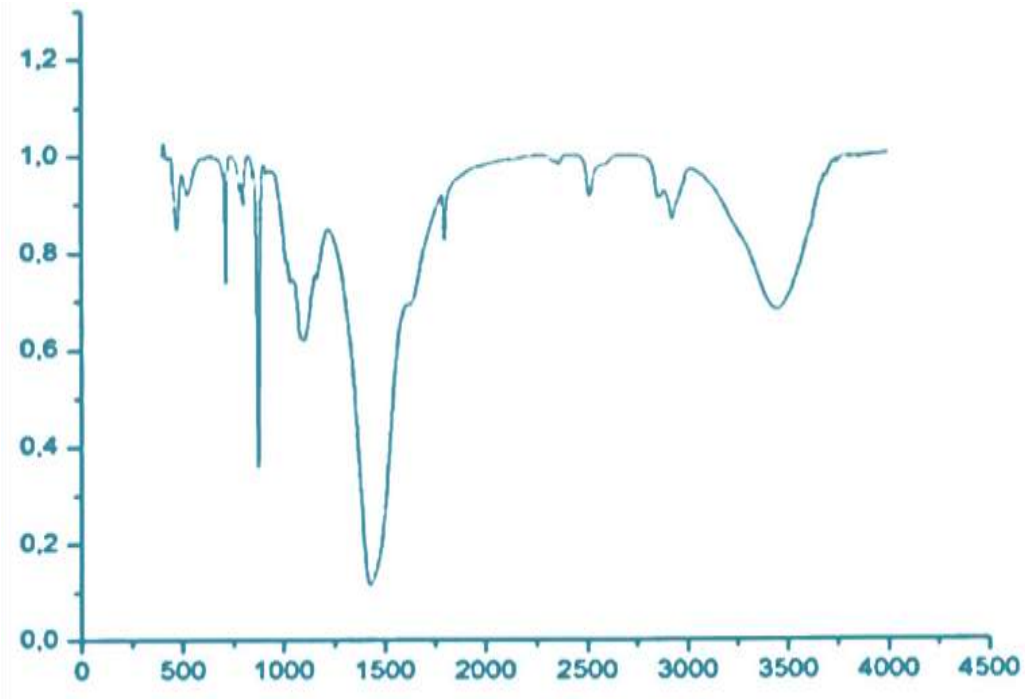

Fig 25:- IR spectrum of the precipitate after filtration of one gram of shale (Z4) solubilized by 50 cm^3 of ocean water at ambient temperature 24, 5°C.

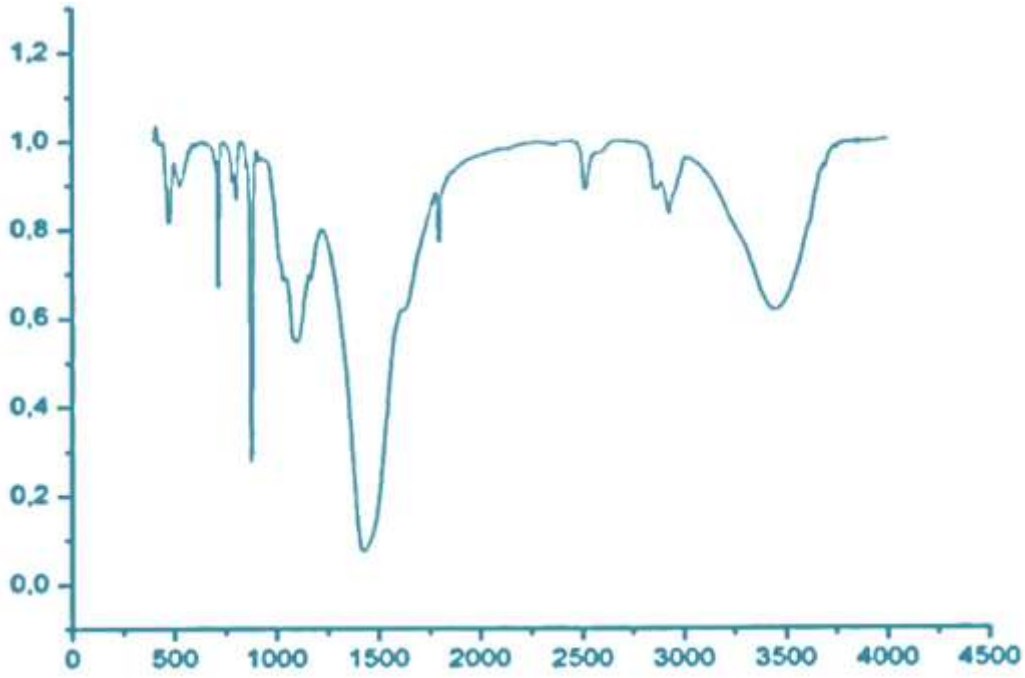

Fig 26:- IR spectrum of the precipitate after filtration of one gram of shale (Z4) solubilized by 50 cm^3 of ocean water at ambient temperature 49°C.

The respective frequencies of 1550 cm^{-1} and 3300 cm^{-1} relate to the aromatic hydrocarbons and the unsaturated aliphatic hydrocarbons, we gather the samples with their absorbance in the following tables:

Table 4:- IR analysis of various samples of oil shale solubilized in Atlantic Ocean water.

1550 cm^3frequency: aromatic	
Sample	Absorbance
Z0 (ambiente)	90
Z0 (T=27,5°C)	86
Z0 (T=49°C)	75
Z4 (ambiente)	86
Z4 (T=24,5°C)	86
Z4 (T=49°C)	92

3300 cm^3frequency : aliphatic	
Sample	Absorbance
Z0 (ambiente)	50
Z0 (T=27,5°C)	38
Z0 (T=49°C)	34
Z4 (ambiente)	34
Z4 (T=24,5°C)	34
Z4 (T=49°C)	38

The absorbance given by the spectral peaks are proportional to the concentrations of compounds identified according to their position.

In the 1500 cm3 region for the Z0 layer, the concentration of aromatics decreases in the precipitate and therefore increases in the filtrate with temperature, so solubility increases in the same direction as temperature (Arrhenius law is verified).

In the 3300 cm3 region (aliphatic), we can see that the same phenomenon described above occurs for Z0.

The Z4 layer is deep, highly reactive and concentrated in high molecular weight hydrocarbons **(Ahmed Malal, Doha Lahmadi and AbdeljabbarAttaoui: 2022).** For temperatures T= ambient and T= 24,5°C, the same absorbance are identified for both aromatics and aliphatic, so these materials decompose by simple agitation insensitively to temperature.

However, at around 50°C, both absorbance increase rapidly, which can only be explained by the fact that from this temperature onwards, we see the start of the decomposition of high molecular weight hydrocarbon compounds with high reactivity into light hydrocarbon compounds (aromatics and aliphatic).

Conclusion:-

Identification by spectroscopy uses radiation of varying energies depending on the compounds to be detected. For example, for infrared, the energy used to identify substituted unsaturated aliphatic is greater than that used to identify substituted unsaturated monocyclic. It should be noted that this energy varies in the same direction as the frequency of the radiation used, whereas frequency is inversely proportional to wavelength. As far as we are concerned, the energy of identification by ultraviolet is sufficiently higher than that of infrared, which means that the compounds to be detected from oil shale can only be heavy hydrocarbons (branched and multisubstituted unsaturated aliphatic chains).

The experimental studies led us to a number of conclusions and results. Firstly, the solubility of oil shale using drinking water is less consistent than when partially distilled water is used (a ratio of around 2/3 between the two cases). Similarly, the energy is lower (slightly higher wavelength) than in the case of distilled water. It should be noted that at low temperatures, drinking water diffuses less energy than distilled water (for the same applied voltage).

At a temperature of 48°C we were able to detect a decomposition reaction (fall in absorbance) in the form of short

chains of substituted unsaturated aliphatic. This reaction occurred for both types of water. The multiplicity of peaks was observed in the case of partially distilled water diffusing heat and highlighting the presence of two types of multisubstituted unsaturated aliphatic, one light and less concentrated than the other and which can only be decomposition in situ: A→B+C.

Finally, for both types of water, the thermal laws are still conceivable, since from 74 0C the solubility increases with temperature.

A considerable part of the Tarfaya deposit is immersed in the Atlantic Ocean. In this part of the work, followed by volumetric complexometric dosing (filtrate) and Infra-Red spectroscopic analysis (precipitate), a study of the solubility of its oil shale by seawater (Atlantic) was carried out.

After solubility under the chosen conditions, the filtrate was measured by complexometry to identify the cations Ca^{2+}, Mg^{2+} (carbonate constituents) and Na^{+}. The first result is that this solubility is accentuated for the Z0 layer (surface layer), thus verifying the thermogravimetric studies **(A. Attaoui et al: 2022)**. Whether for Z0 or Z4 (deep layer), almost the same volumes of the dosage are present, independently of the temperature, up to around T= 50°C. Therefore, under these conditions, simple agitation allows identical solubility of the carbonates up to this temperature.

Infra-red spectroscopic analysis of the precipitate also verifies this solubility for organic matter (kerogen), as well as demonstrating Arrhenius' law for the Z0 layer (aromatics or aliphatic alike). For the Z4 layer, where the material is highly reactive, solubility is identical by simple agitation at low temperatures. Given the high concentration of high molecular weight organic matter in this layer, at a temperature of T=50°C, we can see the start of decomposition of this matter into aliphatic and aromatics (high absorbance).

References:-

[1] T.Funazuri et al,Supercritical fluid extraction of Chinese Maoming oil shale with water and toluene, Fuel 1988,10,vol67,January
[2] G.V.Deshpande, G.D.Bishop,A.A.Gopal and J.Wender, Fuel 1984,63,956
[3] T.J.Houser, D.M.Tiffany, Z.Li, M.E.McCarville and M.E.Houghton, Fuel 1986, 65,827
[4] K.Z.Qin, R.A.Wang and S.S.Jia, Energy Sources 1984, 7,237
[5] Y.Zhu, H.Yang, K.Xiong and W.Xue, Preprint of Pacific Synfuels Con, Tokyo, 1982,Vol1,p.268
[6] Standarrd Oil Company, (Indiana, USA), US patent 1515872, 1978)
[7] J.F.McKay,S.L.Chong and G.W.Gardner, Liquid Fuels Technol,1983,1,299
[8] J.F.McKay and S.L.Chong,Liquid Fuels Technol, 1983, 1,289
[10] T.Funazukuri,K.Mizuta and N.Wakao, Fuel 1988, Vol 67, November, p 1510
[11] H.H.Oelert and R.Siekman, Fuel 1976, 55, 39
[12] P.Bjornbom and E.Bjornbom, Fuel 1987, 66, 77
[13] D.S.Ross, Q.C.Nguyen and G.P.Hum, Fuel 1984, 63, 1211
[14] J.C.Cavalier and F.Chornet, Fuel 1978,57,304
[15] D.S.Ross and J.E.Blessing ,Fuel 978, 57,379
[16] Y.Takemura and K.Ouchi, Fuel 1983,62,1133
[17] J.M.L.Penninger,Elsevier, Amsterdam, 1985,pp,309-329
[18] J.C.Cavalier and E.Chornet, Fuel 197756,57
[19] Y.Takemura and K.Ouchi, Fuel 1983, 62, 1133
[20] L.A.Amestica and E.E.Wolf, Fuel 1986, 65, 1226
[21] R.M.Balduin and K.W.Chen, Fuel Process Techno 1987, 13, 103
[22] AhmedMalal,DohaLahmadiandAbdeljabbarAttaoui,"Typeofburialandadaptationofthegeological ages with the sedimentation of the organic matter for the different layers for the Tarfaya's oilshaledeposit(Morocco)",*Int.J.Adv.Res*.10(04),372-382,April2022,DOI:10.21474/IJAR01/14557.
[23]Awatif. Farah, Nasreddine.Azouaz,Abdeljabbar.Attaoui,Imane.Sadekand Fouzia.Taous,The fivereasonsproving that the Timahdit (Morocco) oil shale deposit is lacustrine, *Int.J.Adv.Res*,2022,DOI**:**10.21474/IJAR01/14743
[24]A.Attaouietal,MineralmatterhydropyrolysisofTarfayaoilshaleandinfluenceofsedimentationedge,*Oil. Shale*.2022Vol,No.4,pp.290-307.Doi: https://doi.org/10.3176/oil.2022.4.04