Analysis and Identification of A Semi-White Soap Bar by Infrared Absorption Spectra and a Reflectance Graph

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Research Article

ABSTRACT

A semi-white colored soap bar was analyzed, and its total fatty matter content, unsaponifiable, unsaponified and unsaponified saponifiable matter content, ethanol-insoluble matter, and free caustic alkali content were determined to be 80.2%w/w, 2.5%w/w, and 0.42%w/w, and 0.096%w/w respectively. The infrared spectra of total lipids, and unsaponifiable fats, were recorded. The Kubelka-Munk K/S value was calculated using the expression depended on reflectivity R_∞ of the observed soap's surface to be K/S=7.8683. The CIE L*a*b* value for the soap bar was found $L^*(C/2)=63.98$, $a^*(C/2)=+6.30$ and $b^*(C/2)=+26.11$. From the diffuse reflectance spectra of the soap bar the band gap energy (E_g) of the material has been calculated to be 1.87409×10^{-19}J for permitted indirect transitions

INTRODUCTION

Base promoted hydrolysis is called saponification, which means soap making. Over 2000 years ago soaps were made by heating animal fat with wood ashes. Animal fat is rich in glycerol triesters and wood ashes are a source of potassium carbonate. Base-promoted cleavage of the fats produces a mixture of long-chain carboxylic acids and their potassium salts. Potassium and sodium salts of long-chain carboxylic acids form micelles that dissolve grease and have cleansing properties. The carboxylic acids obtained by saponification of fats are called fatty acids. The greases in general, fat and oils are of natural origin. They contain the triesters of long chain carboxylic acids. Like all esters, they are hydrolysed (saponified) by alkalis. Long chain carboxylate anions of the type formed here have detergent properties because the product of saponification of a fat is soap. Thus alkalis not only break down fats but they turn them into soap. Vegetable oils are associated with the manufacturing of high quality natural soaps [1].

In this work a pure soap made from olive oil was analyzed. It was a boiled soap cooked with 100% virgin olive oil, soft water and sodium derived from sea salt. The soap was formulated by the hot process for sodium salts. It is called the hot saponification process. This soap is a mixture of sodium salts of various naturally occurring fatty acids. The saponification is the process in which triglycerides are combined with a strong base to form fatty acid metal salts during the soap –making process [1].

RESEARCH METHODOLOGY

In this work the properties of a semi-white soap bar were determined, such as pH [2], infrared spectra, and uv-visible spectroscopy study [3].

Soaps act as cleansers because the two ends of a soap molecule are so different. The sodium salt end of the long-chain molecule is ionic and therefore hydrophilic; it tries to dissolve in water. The long hydrocarbon chain portion of the molecule

however is nonpolar and lipophilic; it tries to dissolve in grease. The net effect of these two opposing tendencies is that soaps are attracted to both grease and water and are therefore valuable as cleansers.

When the soap is dispersed in water the long hydrocarbon tails cluster together in a lipophilic ball, while the ionic heads on the surface of the cluster stick out into the water layer. These spherical clusters are called micelles. Grease and oil droplets are solubilized in water when they are coated by the nonpolar tails of the soap molecules in the center of micelles. Once solubilized the grease and dirt can be rinsed away.

The semi-white soap bar was analyzed and characterized in this work as a finished product. The soap bar is generally considered as an anionic surface active agent. As a consequence an understanding then of the detergent parameters that determine solubility and functionality is crucial to the continued understanding of integral membrane proteins. By careful consideration of anionic detergents, such as soaps, lipids and reaction conditions, the techniques that seem trivial when applied to water soluble proteins can also find their uses in the elucidation of the structure and functionality of membrane proteins [4].

Reagents

All the chemicals were of analytical reagent grade quality and they were used without further purification. Solutions were prepared using deionized water of conductivity <1µS/cm. Ethanol absolute anhydrous (1L) was procured from Carlo Erba UN1170 was gradient grade. The ethanol 95%v/v solution was prepared and neutralized to the phenolphthalein solution. Sulphuric acid RPE 0.5M (1N) for analysis was procured from Carlo Erba UN 2796. Sodium hydroxide 0.1N (N/10) for analysis was procured from Carlo Erba UN 1824. Potassium hydroxide (KOH) 1Kg M.W.:56.11, DAB 6, B.P.1968 was procured from ERFAR. Potassium hydroxide approximately 0.5N standard volumetric solution in ethanol was prepared. Methyl orange 0.2%w/w solution was prepared. Phenolphthalein 1%w/v solution in ethanol 95° was prepared. Light petroleum ether, boiling range between 40°-60°C RPE for analysis was procured from Carlo Erba UN 1268.

Apparatus

IR spectra were obtained on Perkin Elmer Inc FTIR Spectrometer, Spectrum 2000 Version 5.0.2 Copyright 2004 using an ATR crystal. Absorption spectra of the soap bar material were obtained by means of a Spectrophotometer CM-3630 BCMTS M Type 40605, S.N. 43029, TouchScreen-M V 2.0, Frank-PTI. pH measurements were made using a calibrated pH-meter Metrohm 716 DMS Titrino, Swiss made. The pH electrode was first calibrated with standard buffer solutions with known pH values that spanned the range being measured i.e. pH 4, pH 10, and pH 7. Weighings were carried out on an analytical balance Mettler Toledo AB 204-S/FACT accurate to 0.1mg, maximum capacity 220g. The petroleum ether solutions were evaporated on a water bath FALC, 220/240V, 50Hz. The oven used was Memmert direkt, capable of being controlled at $103^0C \pm 2^0C$.

Ordinary laboratory apparatus were used i.e. Beakers of capacity 250 ml, three separating funnels capacity 500 ml, conical flasks of capacity 250 ml.

Sample preparation

The sample of the semi-white soap was analyzed directly and no sample preparation was required on the finished product.

SOAP ANALYSIS

Determination of the total fatty matter content of the soap [5]

We weighed 5.0015g of the semi-white soap into a 250 ml beaker. We then dissolved the test portion in 100 ml of hot water and we poured the solution into one of three separating funnels. We washed the beaker with water nearly 50 ml and we added the washings to the first separating funnel. We added a few drops of the methyl orange solution and then from a burette we added, while vigorously shaking the separating funnel, 20 ml of a 1 N (0.5 M) sulphuric acid solution until the color of the solution changed from yellow to pink. We then cooled the contents of the separating funnel to about 25°C and we added 100 ml of light petroleum ether. We gently shaked it and released the pressure. We repeated the shaking until the aqueous layer became clear and we then allowed to stand. Then we ran off the aqueous layer into the second separating funnel and we extracted with 100 ml of the light petroleum ether. We repeated the process of the extraction with 50 ml of the light petroleum ether into a third separating funnel and we combined the three light petroleum extracts in the first separating funnel. We then washed the light petroleum extract by shaking with 30 ml water until the washings were neutral to the methyl orange solution. We carried out three washings with 30 ml of water each. We evaporated off all of the washed light petroleum solutions in a glass container weighing 108.9910 g on the water bath. We then heated the container with the residue to constant mass in the oven for 1hr. We finally cooled in a desiccator for 40min, and we weighed the contents to be 113.0030 g.

Yield: 4.0120g of total fatty matter for the semi-white soap, i.e., yield: 80.2% w/w,

The yield was calculated as the following formula:

$$Yeild = \frac{mass\ of\ total\ fatty\ matter\ in\ g\ x\ 100}{mass\ of\ soap\ weighed\ in\ g} = \frac{4.0120g\ x\ 100}{5.0015g} = 80.22\%w/w \quad (1)$$

Then the Yield for the saponified fatty matter content is:

Total fatty matter - (unsaponifiable, unsaponified and unsaponified saponifiable matter)=80.22% w/w-2.497% w/w=77.7% w/w (3)

Determination of content of ethanol-insoluble matter [6]

We weighed 5.0162g of the semi-white soap into a 250 ml beaker. We added 150 ml of the ethanol 95% v/v, previously heated to near its boiling point and neutralized using phenolphthalein indicator and four (4) drops of 0.1 N NaOH solution, in the beaker, and heated on the water bath. We have dried before the filter paper to be used for the filtration of the insoluble matter in the oven for an hour. We allowed to the filter paper to cool to ambient temperature in a desiccator for 20min, and we weighed it to be 1.0872 g. We then placed it in a funnel mounted on a conical flask placed on the water bath. When the soap was completely dissolved we decanted the supernatant liquid on the filter paper and then washed the insoluble matter in the conical flask by decantation with ethanol previously heated to near its boiling point and neutralized using phenolphthalein indicator and three (3) drops of 0.1 N NaOH solution, and we transferred the insoluble matter to the filter paper with small quantities of this warm ethanol. The filter paper and the residue were washed with the warm ethanol until entirely free from the soap. We finally dried the filter paper in air and we placed it in the oven. After 1 h, we removed the filter paper and left it in the desiccator for nearly 20min, and we weighed it to be 1.1084 g.

Yield: 0.0212g (1.1084g-1.0872g=0.0212g), i.e. 0.42%w/w for the semi white soap

The yield was calculated as the following formula:

$$YIELD = \frac{mass\ of\ ethanol\ insoluble\ matter\ in\ g\ x\ 100}{mass\ of\ soap\ weighed\ in\ g} = \frac{0.0212g\ x\ 100}{5.0162g} = 0.423\%w/w \quad (4)$$

Determination of free caustic alkali [7]

In the ethanol solution of the above filtrate were added four (4) drops of phenolophthalein indicator and the color of the solution was kept colored pink, and 1.2 ml of a 0.1N HCl solution was added to it until it became colorless. The free caustic alkali was expressed as sodium hydroxide.

The yield was 0.096% w/w NaOH for the semi-white soap. The yield was calculated as the following formula:

$$YIELD = \frac{ml\ of\ HCL\ used\ x0,1eq/ltx100xMWNaOH}{1000\ ml\ in\ Ltxmass\ of\ soap\ weighed} = \frac{1.2ml*0.1N*10^{-3}*100*40g/mol}{5.0162g} = 0.0957\%w/w \quad (5)$$

The free caustic alkali is expressed as sodium hydroxide for sodium soaps and the above method can only be applied to pure soaps made from olive oil.

RESULTS AND DISCUSSION

Determination of pH

We prepared a 1%w/w solution of the semi-white soap in deionized water and we measured pH 10.65 at a temperature of 26.11°C (299.27K) in the Metrohm 716 DMS Titrino pH-meter. We measured the pH of the buffer solution pH 7 as it is to be pH 7.18 at 26.1°C (299.27K) in the Metrohm 716 DMS Titrino pH-meter. At this pH 10.7 the fatty acids of this soap in water and in phospholipid bilayers were approximately at almost complete-ionisation.

Acquisition of IR-spectra

Infrared Transmittance data: The infrared spectra were recorded in the solid state. The material of the ATR (Attenuated total reflection) [8] crystal was diamond.

In the above spectrum **(Figure 1)** a strong C=O stretching absorption band in the peak 1555cm^{-1} is due to carboxylic acids, and carboxylic esters present in the soap bar. Its relatively constant position, high intensity, and relative freedom from interfering bands make this one of the easiest bands to recognize in IR spectra of soaps. In general the carboxylate ion group absorbs strongly near 1600cm^{-1}-1590cm^{-1}. These bands result respectively from asymmetrical and symmetrical (C=O)$_2$ stretching. The C=O absorption band of saturated aliphatic esters is in the peak 1728cm^{-1}.

The α,β-unsaturated and aryl conjugated acids show absorption of the dimer in the 1708 cm^{-1} peak **(Figure 2)**. In general the C=O group in dimerized saturated aliphatic acids absorbs in the region of 1720-1706 cm^{-1}. The carboxylate ion gives rise to two bands: a strong asymmetrical stretching band near 1650-1550cm^{-1} here in the 1646 cm^{-1} peak, and a weaker symmetrical stretching band near 1400 cm^{-1}, here in the 1459 cm^{-1} peak [9]. Two bands arising from C-O stretching and O-H bending appear in the spectra of carboxylic acids near 1440-1395cm^{-1} and near 1320-1210 cm^{-1}, here in the 1440 cm^{-1} peak, and in the 1260 cm^{-1} peak (not marked in the spectrum).

The C=O absorption band of saturated aliphatic esters appears in the 1733cm^{-1} peak **(Figure 3).** The shifting in general of the C=O absorbance band of unsaponifiable fats in soaps is due to changes in the structural features of the respective molecules,

which follows the degree to which the molecules absorb radiation is also affected. The O-C-C band of esters of primary alcohols occurs at 1064-1031cm^{-1} here in the 1031cm^{-1} peak. Also the C-(C=O)-O band of saturated esters appears at 1160cm^{-1}. The C-C(=O)-O stretch of esters of α,β-unsaturated acids results in multiple bands in the 1300-1160cm^{-1} region. Here it appears in the 1160cm^{-1} peak.

Calculation of Kubelka-Munk K/S values for the two soaps (absorption coefficient/scattering coefficient ratio)

The K/S ratio for the semi-white soap was found K/S=7.8683 (6) and the reflectance ISO brightness used was measured 17.68% [10] **(Figure 4).** The ISO brightness measured is the numerical value of the reflectance of the soap bar at 457nm, blue light reflectance.

In this work the Kubelka-Munk theory is used for predicting optical properties for the semi-white soap bar **(Table 1).** The appearance of a soap bar is the result of its optical properties. As known the Kubelka-Munk theory is based on the assumption that the interaction between the diffuse light and the soap material can be described in terms of two fundamental optical constants. The specific scattering coefficient (S) and the specific absorption coefficient (K). Although the Kubelka-Munk theory holds strictly
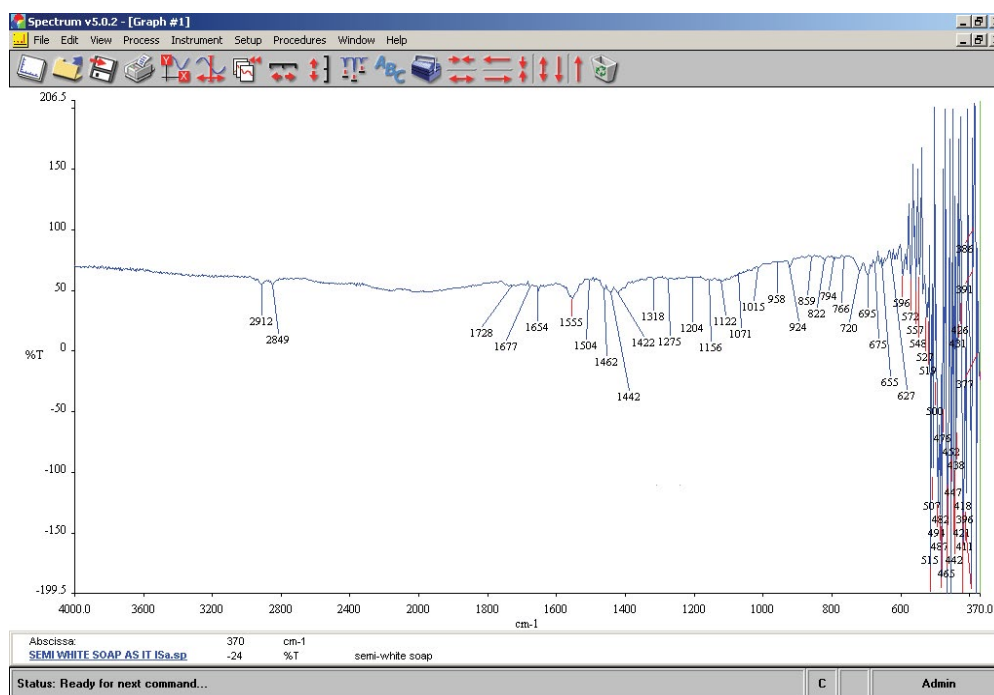

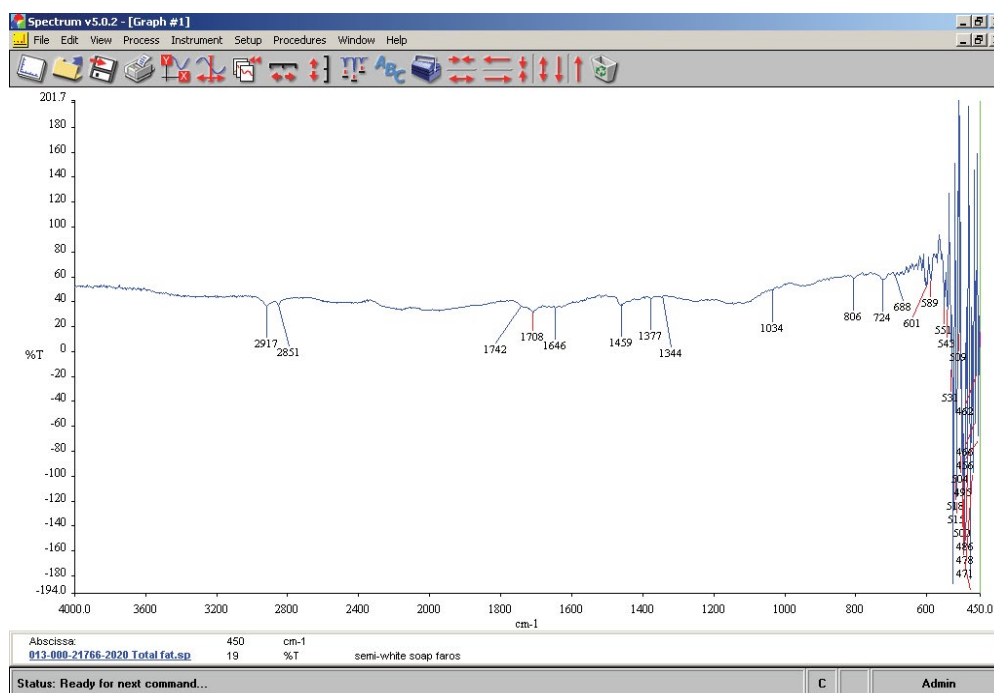**Figure 1.** FT-IR spectrum of the semi-white soap bar as it is.

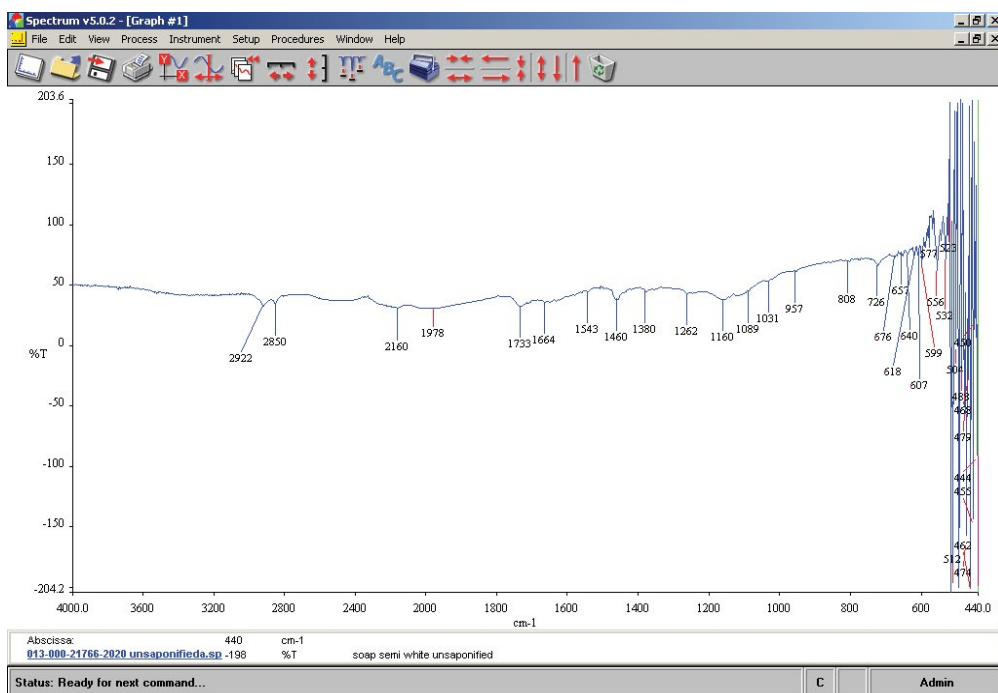**Figure 2.** FT-IR spectrum of total lipids in the semi-white soap bar.

Figure 3. FT-IR spectrum of unsaponifiable, unsaponified and unsaponified saponifiable matter in the semi- white soap.
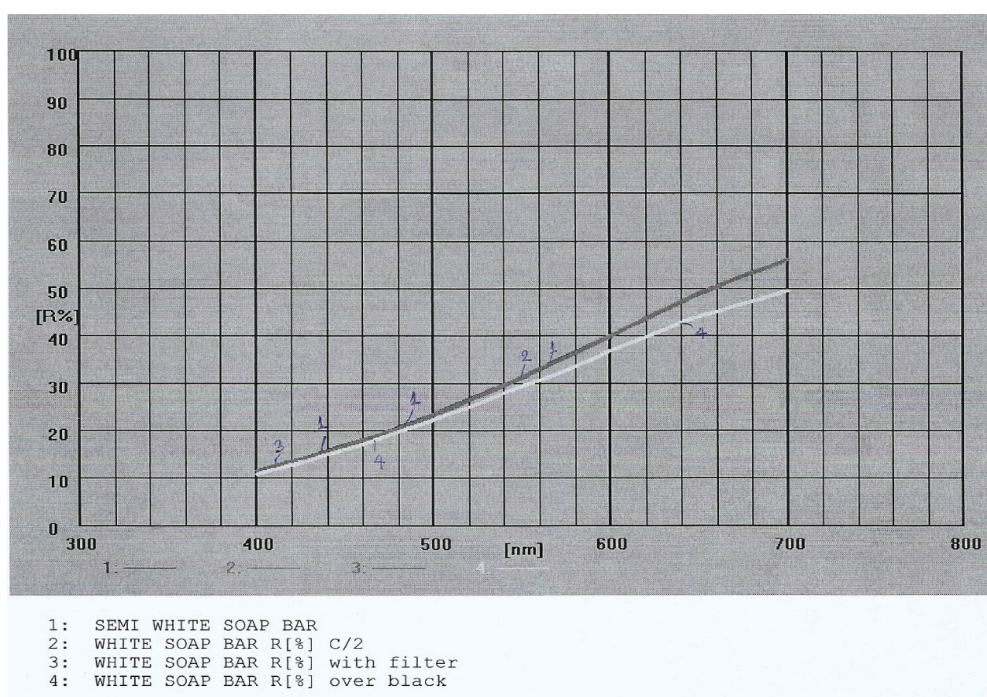

1: SEMI WHITE SOAP BAR
2: WHITE SOAP BAR R[%] C/2
3: WHITE SOAP BAR R[%] with filter
4: WHITE SOAP BAR R[%] over black

Figure 4. DRS spectrum of the semi-white soap bar as it is.

Table 1. Optical properties for the semi-white soap bar.

Variables	L*(C/2)	a*(C/2)	b*(C/2)	ΔE*
Calibration standard	96.67	-0.152	-0.295	--
Semi-white soap bar	63.98	6.3	26.11	42.149

for homogeneous materials only, it works also for soap bars containing more than one substances. The equation of Kubelka-Munk used above is: $K/S = (1-R_\infty)^2/2R_\infty$ (7) where K is the absorption or coefficient of reflectivity and S is the coefficient of light scattering; R_∞ is the observed reflectivity for monochromatic light. The simplified equation $F(R_\infty) = (1-R_\infty)^2/2R_\infty = K/S$ (8) is used in order to relate the chromophore concentration present to the intensity of the sample's diffuse reflection. The chromophores present in this study are the carbonyl group (C=O) and a conjugated pi-system.

Some optical and physical properties of the semi-white soap bar were determined also i.e. its ISO brightness value, its opacity value and its pH value as well as its moisture content and weight. The ISO brightness (ISO 2470-1) [11] of the semi-white soap bar was measured 17.68%. Its opacity value (ISO 2471) [12] was calculated as 92.90%. The pH of the soap's 1%w/w solution

in water (EN ISO 1262/1996) [13] was measured pH=10.65 at a temperature of 26.1°C (T=273.16°C+26.11°C= 299.27K). The moisture content of the soap bar (ISO 287/2017) [14] was determined as 1.3%w/w. Also the soap bar as it was, weighed 139.6g.

From the two K/S ratio calculated above we can assume that light absorption is high in the semi-white soap bar than in other soap bars tested previously indicating the presence of more colored matter other than soap which is converted to heat thereby reducing the brightness of the semi-white soap bar.

$CIE\ L*,\ a*,\ b*$ values for the semi-white soap bar analyzed

The color of the semi-white soap bar in the $CIE\ L*,\ a*,\ b*$ system for illuminant C/2 is L*=63.98 a*=6.30 and b*=26.11. L is the measure of lightness and varies from 100 for a perfect white to 0 for the absolute black. Here +a indicates the redness of the soap bar and +b indicates its yellowness. The opacity calculated for the semi-white soap is 92.90% and the transparency is 25.27%.

In the **Table 1** $CIE\ L*,\ a*,\ b*$ values for the soap bar sample are presented, as well as of the calibration standard used, and the $\Delta E* = [(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2]^{1/2}$ (9) value is calculated, whereas $L*(C/2)a*(C/2)b*(C/2)$).

In the above **Table 1,** the $CIE\ L*,\ a*,\ b*$ values for the semi-white soap bar analyzed and the calibration standard are presented. With the use of this color system the magnitude and direction of color difference between the semi-white soap bar sample and the calibration standard used was determined. The Delta E ($\Delta E*$) value is overall color difference value which takes into account lightness/darkness differences as well as chromatic differences. The intended object of the $CIE\ L*,\ a*,\ b*$ system for illuminant $C/2$ is of a color difference ($\Delta E*$) of 1.0 unit to be exactly the same visual color difference anywhere in color space. This objective is not realized here. In practice this objective is seldom realized therefore the establishment of tolerance based on ΔE is not usually used.

Estimation of the band gap energy E_g from the DRS studies of the semi-white soap bar

A graph is plotted of $hv - (K/S\ hv)^2$ **(Figure 5).** The extrapolation of the straight line to $(K/S\ hv)^2 = 0$ axis (Tauc Plot) produces the value of the band gap energy (E_g) for permitted indirect transitions n=2. The estimation of the band gap energy is performed from a DRS (Diffuse reflectance spectra) study. The band gap energy between HOMO and LUMO (E_g) [15-19] of the chromophores present in the semi-white soap bar as it is, was calculated and was found to be 1.169806978eV [20-22] or $1.87409x10^{-19} Joules$. The value of the band gap energy of the material was estimated by extrapolating the straight line to ($\alpha hv)^2$=0 axis (Tauc plot), in the graph at K=0, i.e. from the function trend in the excel spreadsheet, with data calculated for the whole range of wavelengths 400-700nm. Comparison with previous results on the optical band gap energy estimation verified that the optical band gap value was decreased when the pH value of the cleaner or soap was increased (pH>9) [23]. When we measured here the gap optically we used excitation spectroscopy. Thus the minimum frequency of light that would dislodge an electron from the semi-white soap bar was calculated as $v= \dfrac{1.87409x10^{\wedge} -19J}{6.626x10^{-34} J.s} = 2.82838816x10^{14} S^{-1}$ (10). The maximum wavelength of light that would then dislodge i.e. promote the electron from the filled band to the empty band in the soap bar was then approximately $\lambda = \dfrac{2.9979x10^8 m/s}{2.82838816x10^{\wedge}14s} = 1059.932nm$ (11) [24].
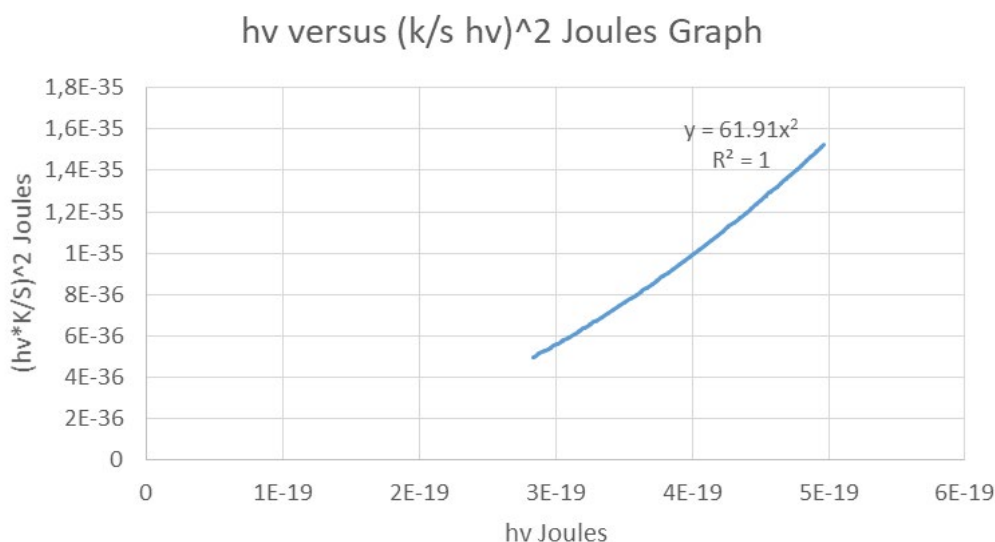

Figure 5. hv versus (K/S hv)2 graph of the chromophores C=O and conjugated pi-system of the semi-white soap bar, for permitted indirect transitions n=2.
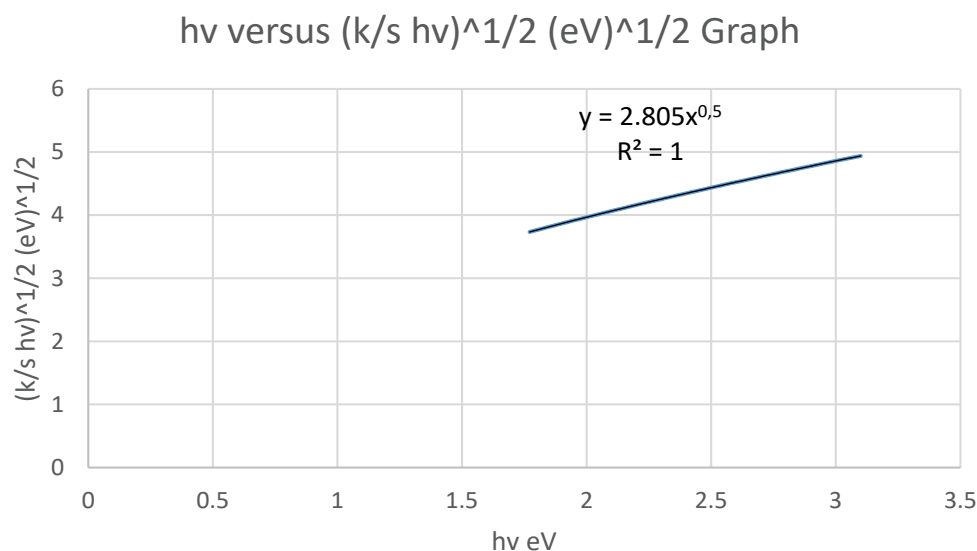
hv versus (k/s hv)^1/2 (eV)^1/2 Graph

Figure 6. hv versus $(K/S\ hv)^{1/2}$ graph of the chromophores C=O and conjugated pi-system of the semi-white soap bar, for permitted direct transitions n=1/2.

The band gap energy (E_g =hv) is a characteristic feature of all materials which determines their application potential. It depends on the material as well as its special characteristics like crystallinity and stoichiometry. The band gap energy can be determined using the following formula $E_g = hv = \dfrac{hc}{\lambda}$ (12) where h is Planck's constant $(6.626 x 10^{-34} J.s)$, c is the velocity of light $(2.9979 x 10^{8} m / s^{-1})$ and λ is the absorption wavelength (nm) and the frequence v of the radiation is given by v.λ=c (13).

The band gap was obtained from optical absorption edge energy which is defined as the minimum photon energy required to excite an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [25].

A graph is plotted also of hv - $(K/S\ hv)^{1/2}$ **(Figure 6).** The extrapolation of the straight line to $(K/S\ hv)^{1/2} = 0$ axis produces the value of the band gap energy (E_g) for permitted direct transitions $n = 1/2$, to be 2.141114 eV. Electronic transitions are of two types-direct and indirect. Direct transitions require only that photons excite electrons, whereas indirect transitions require concerted vibrations and energy from the crystal lattice (phonons).

CONCLUSION

Diffuse reflectance spectrum of the soap bar was recorded. From the DR spectrum, the energy band gap of the material was estimated using the Kubelka-Munk equation. In conclusion, the FTIR method and the Reflectance graph, are simple, accurate and easily applicable methods to the identification of finished products of anionic surfactants and soap samples. Presently, we are investigating the use of FTIR for a wide variety of detergent, and cosmetic finished products.

REFERENCES

1. Vidal NP, et al. The Effects of Cold Saponification on the Unsaponified Fatty Acid Composition and Sensory Perception of Commercial Natural Herbal Soaps. Molecules. 2018;23:1-20.

2. Cistola DP, et al. Phase Behavior and Bilayer Properties of Fatty Acids: Hydrated 1:1 Acid-Soaps, Biochemistry. 1986;25:2804-2812.

3. Kuntom A, Kifli H, and Lim PK, Chemical and physical characteristics of soap made from distilled fatty acids of palm oil and palm kernel oil. J.Am.Oil Chem.'Soc. 1996;73:105-108.

4. Seddon MA, Curnow Paul, Booth PJ, Membrane proteins, lipids and detergents:not just a soap opera.BBA.2004;1666:105-117.

5. ISO 685 First edition: Analysis of soaps-Determination of total alkali content and total fatty matter content 1975.

6. ISO 673 Second edition: Soaps-Determination of content of ethanol-insoluble matter 1981.

7. ISO 456 First edition: Surface active agents – Analysis of soaps-Determination of free caustic alkali 1973.

8. Zhao L, et al. Spectral Radiative Properties of a Liquid n-Octane Droplet in the Midinfrared Region,J SPECTROSC.2020.8890265:1-9.

9. Gomez A M P, et al. Copolymer Based on Polyglycerol-Acrylate-Lactate as Potential Water Viscosifier and Surfactant for Enhanced Oil Recovery, Int. j. polym. sci. 2020.3464670:1-9.

10. Shahin A, Bachir W, and Daher E MS. Polystyrene Microsphere Optical Properties by Kubelka-Munk and Diffusion Approximation with a Single Integrating Sphere System: A Comparative Study J. Spectrosc. 2019 .3406319:1-8.

11. ISO 2470-1: Paper, board and pulps-Measurement of diffuse blue reflectance factor –Part 1: Indoor daylight conditions (ISO brightness) 2016.

12. ISO 2471: Paper and board-Determination of opacity (paper backing)-Diffuse reflectance method 2008.

13. EN 1262: -Surface active agents-Determination of pH value of solutions or dispersions 2003

14. ISO 287: Paper and board-Determination of moisture content of a lot –Oven drying method 2017.

15. Stankevich V.V, et al. Optical properties of Multilayer Heterostructures based on zinc chalcogenides upon strong Laser Excitation, J. Appl. Spectrosc. 2007.74:897-902.

16. Raftani M, et al. Theoretical study of new conjugated compounds with a low bandgap for bulk heterojunction solar cells: DFT and TD-DFT study. Results Chem 2020;2:100040.

17. Astasauskas V, et al. Optical and electronic properties of amorphous silicon dioxide by single and double electron spectroscopy, J Electron Spectros Relat Phenomena. 2020;241:146829.

18. Kumar H, et al. Polyaniline-metal oxide-nano-composite as a nano-electronics, opto-electronics, heat resistance and anticorrosive material. Results Chem. 2020;2:100046.

19. Saaed W, et al. Catalyst-and organic solvent-free synthesis, structural, and theoretical studies of 1-arylidenamino-2,4-disubstituted-2-imidazoline-5-ones. Results Chem.2020;2:100042.

20. Chryssou K, et al. Analysis of a Product Cleaner for Car Windows and Identification of its Surfactants by Infrared Absorption Spectra and calculation of Band Gap Energy by its Reflectance Graph. Ann. chem. sci. res. 2020;2:1-7.

21. Hone FG and Dejene FB. Cationic concentration and pH effect on the structural, morphological and optical band gap of chemically synthesized lead sulfide thin films. J. Mater. Res. 2019;8:467-474.

22. Ikhmayies S.J, Riyad N. Ahmad-Bitar. A study of the optical bandgap energy and Urbach tail of spray-deposited CdS:In thin films. J. Mater. Res. 2013;2:221-227.

23. Devidas G. B., et al. Effect of Deposition Period and pH on Chemical Bath Deposited PbSe Thin Films. Adv. Appl. Sci. Res. 2016;7:200-204.

24. Tan TL, et al. Tunable Band Gap Energy of Mn-Doped ZhO Nanoparticles using the Coprecipitation Technique. J. Nanomater.2014;371720:1-6

25. Shiraishi Y, et al. Fluorometric and colorimetric detection of hypochlorous acid and hypochlorite by a naphthalimide-dicyanoisophorone conjugate J. Photochem. Photobiol. A. 2021;406:112997.